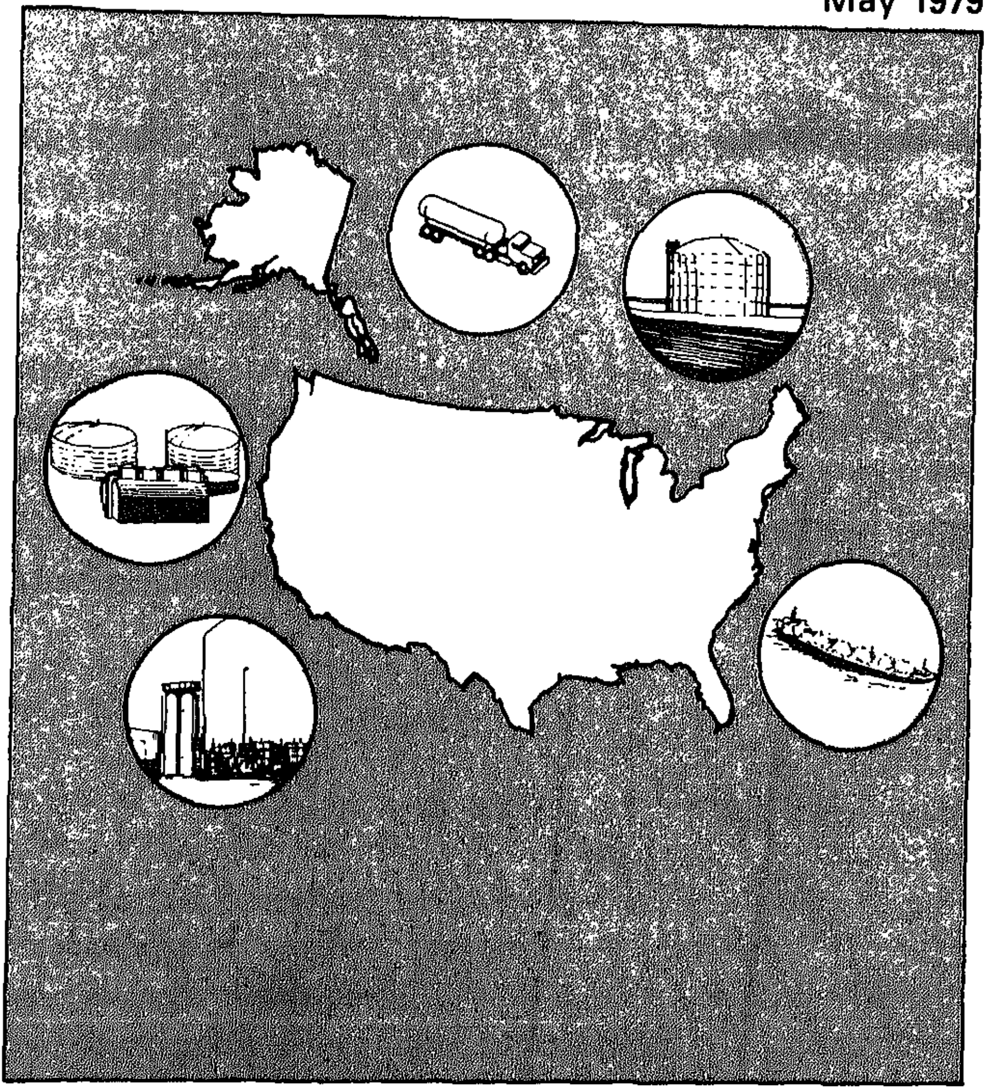
Report

May 1979



U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Environment
Division of Environmental Control Technology
Washington, D.C. 20545

Jet Propulsion Laboratory	NAS-7-100
Lawrence Livermore Laboratory	W-7405-ENG-48
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nt of Energy. The Program is coordinated among the following:

artment of Commerce
itime Administration

artment of Transportation
st Guard
eral Railroad Administration
ice of Pipeline Safety Regulations

Aeronautics and Space Administration

ilizer Institute

Research Institute

ument was compiled by Pacific Northwest Laboratory, operated by rial Institute, who is assisting the Division of Environmental ology in the development and planning of this program.

ergy systems. The need for developing a safety and environmental essment for liquefied gaseous fuels was identified by the Environmental Control Technology as a result of discussions with ernment, industry, and academic persons having expertise with the particular materials involved: liquefied natural gas, etroleum gas, hydrogen, and anhydrous ammonia.

ocument reports on both the current planning and overview aspects efied Gaseous Fuels Safety and Environmental Control Assessment ctions I and II, prepared by the Environmental Control Technology nd on progress made in FY 1978 in technical areas by Government (The Reports). All contractor reports are here printed for the except for Report M, published by Lawrence Livermore Laboratory r 1978 as UCRL-52570.

ports were prepared for the Government under a variety of

t Energy Conversion Company	EP-78-C-03-2057
d Technology Corporation	EP-78-C-05-6020
D. Little, Inc.	EP-78-C-02-4734
opulsion Laboratory	NAS-7-100
ce Livermore Laboratory	W-7405-ENG-48
amos Scientific Laboratory	W-7405-ENG-36
husetts Institute of Technology	EE-77-S-02-4204 EE-77-S-02-4447 EE-77-S-02-4548
Weapons Center	EE-77-A-28-3248 MIPR Z-70099-8-816817A
c Northwest Laboratory	EY-76-C-06-1830

of other fuels. For example, the volume reduction of about 600, y liquefying natural gas, has important transportation and storage ns. The storage of liquefied natural gas (LNG) at critical regional (peakshaving and satellite facilities) within the United States can ural gas during seasonal periods of high demand and during emergencies sources of energy are disrupted. Liquid and liquefied energy are essential in many industrial systems and processes and the avail- these materials is important to both the economy and security of .

epartment of Energy (DOE) has responsibilities to develop a National n and to implement comprehensive research, development and demon- RD&D) programs designed to achieve solutions to short- and long-term ply and management problems (PL 95-91). A portion of the National 77-1, page 32) has the objective of identifying and characterizing cal, health, and safety issues and public concerns associated with cial operation of specific energy systems. The DOE Division of tal Control Technology (DECT) has responsibility for preparing assess- ome of these areas, including liquefied gaseous fuels.

fill this responsibility the DECT is sponsoring a broad spectrum of n safety and environmental control aspects of liquefied gaseous e objective of this effort is to gather, analyze and disseminate information that will aid future decisions made by industry, agencies and the general public relating to facility siting, rations and accident prevention. This research addresses a definable dditional information in this area and complements related programs by other government agencies and industry.

The need for a comprehensive integrated RD&D program to resolve lic
gaseous fuel issues has been identified by the DECT as a result of discu
with many experts from government, industry and academia. The developme
of a program specifically addressing LNG issues began in late fall 1976,
building on information developed in a cooperative program with the U.S.
Guard and the American Gas Association. Further input came from an ERDA
sponsored LNG Safety and Control Workshop (December 1976) which was atte
by over 40 persons selected to represent a cross section of cognizant ex
In the meantime many of the safety and environmental issues identified f
LNG appear to apply to the handling of other liquefied gaseous fuels and
energy materials.

The purpose of this program is, therefore, to develop additional sa
and environmental control information on LNG and other significant lique
gaseous fuels and energy materials. The emphasis of this effort is on
mation needed by industry, regulatory bodies and the general public for
decisions relating to the handling, transportation and storage of these
materials. Section II of this report contains an outline of the DOE Pr
Plan describing the major elements of effort needed to achieve the progr
objectives.

I.2 SUMMARY OF REPORTS

The DOE/DECT Liquefied Gaseous Fuels Safety and Environmental Contr
Research Program currently consists of coordinated program and subprogra
research activities being conducted at four national laboratories and tw
technical institutions with the involvement and support of four industri
research contractors. Section III of this report contains 22 independen
reports (Reports A through V) that provide a detailed summary of progres
achievements in these areas of activity. The scope of the program incl

ents.

fied Natural Gas

report - "An Approach to Liquefied Natural Gas (LNG) Safety and Control Research" (DOE/EV-0002) identifies two distinct objectives goals of the integrated program:

Predictive Capabilities

velop and validate analytical models necessary to equately describe, from a safety and environmental ntrol viewpoint, the behavior of LNG systems and e possible effects of LNG releases to the environnt.

Control Methods

vestigate and validate methods to prevent and ntrol the release of LNG.

six technical areas have been identified as necessary to achieve ves: Vapor Generation and Dispersion, Fire and Radiation Hazards, tion, Release Prevention and Control, Instrumentation and velopment, and Scale Effects Experiments.

on LNG is reported in Section III in reports A through P. These summarized and categorized below according to their relevant tech-

neration and Dispersion

ports are contained in Section III that describe research on LNG ion and dispersion. A model for the unconfined spreading and f LNG when spilled on a water surface has been developed in studies ivermore Laboratory (LLL). As described in Report A, the model

nducted at China Lake have been made and compared with experimental data

Report B describes the comparison of different models used to predict spersion which is another part of the program effort conducted by LLL. ypes of models are reviewed. The first is a version of one originally pr osed by Germeles and Drake; and the second type is in the form of two fin fference codes, MINT and TDC, which solve the time dependent, compressib onservation equations with turbulence. Results of these models are compa n terms of the predicted maximum distance to the lower flammability limit s a function of liquid spill volume. Characteristic vertical profiles of he models are also compared for a particular spill size.

Report C contributed by Pacific Northwest Laboratory (PNL) describes est cases for the evaluation of LNG vapor generation and dispersion model his report presents a systematic approach for comparing LNG vapor generat nd dispersion models using detailed descriptions of the models and the esults produced by the models in selected test cases. A form for recordi odel description information has been developed to ensure uniformity of d nd a standard format for the information. Analytical test cases were sel ased on experimental design methods in an attempt to minimize the number est cases required to study main parameter effects and parameter interact

Fire and Radiation Hazards

The study of radiation from burning hydrocarbon clouds conducted by t assachusetts Institute of Technology (MIT) is described in Report D. This ffort addresses the measurement and analysis of time resolved thermal radi ion from the combustion of methane, ethane, and propane clouds formed fro aboratory scale vapor samples. The time scale of the radiant heat pulse ound to be the same as that of the fluid mechanical motion (Fay and Lewis, 976). The time-integrated radiant energy flux, expressed as a fraction of

gas temperature decreased monotonically during and after the period
bustion. The absorption coefficient was found to be a function of t
fuel volume and fuel type; it was between 10^{-3} and 10^{-2} cm^{-1} and dec
slightly with increasing initial fuel volume.

Flame Propagation

Report E reviews some of the computational models used in the a
of the detonation and deflagration properties of liquefied energy fu
performed at LLL. These models include shock wave hydrodynamics des
and detailed chemical kinetic reaction mechanisms for the specific f
be studied. Chemical induction times are calculated using the detai
kinetic models for fuel mixtures typical of LNG. These times are th
with characteristic shock decay time computed from high explosive ch
detonations to arrive at a quantitative measure of fuel detonability
effects of minor species in the initial fuel sample, of impurities s
water vapor, of fuel-air equivalence ratio, and turbulent mixing on
times and detonability have been investigated.

Release Prevention and Control

Report F discusses efforts by PNL to develop an adequate unders
of LNG release prevention and control systems and the factors which
them. Three basic interrelated work areas (system definition, safet
and data gathering) are considered in this effort. This report cont
liminary results of an assessment of the release prevention and cont
of a generic LNG peakshaving plant. Early results indicate that mor
detailed safety analyses should concentrate on the LNG storage and v
systems.

The reduction of LNG tanker fire hazards is addressed in Report
accounts for effort undertaken by Arthur D. Little, Incorporated. M

uppressants as a means of diminishing tanker fire hazards. Additionally, ystems were considered for protecting the LNG tanker and its crew from the hermal effects of a large fire and for disposing of the cargo in a damaged r disabled tanker.

Report H summarizes effort by the Aerojet Energy Conversion Company to haracterize process, flow and use properties of gelled LNG. This report resents a brief discussion of the development and the state-of-the-art of elled LNG and the potential benefits to be obtained from gelation.

Instrumentation and Technique Development

Four reports are included that describe the development of research nstrumentation and measuring techniques. The detection of atmospheric met s under study at MIT and is documented in Report I. Emphasis is placed on nstrument concepts suitable for detecting methane concentrations between .1% and 100% that may be encountered in spills of LNG or ruptures of flamm as containment vessels. A prototype instrument suitable for use in field ests of LNG dispersion is described. The instrument uses a HE-Ne laser perating at 3.39 μm to product two beams at slightly different wavelengths ne wavelength is strongly attenuated by methane whereas the other suffers egligible attenuation and serves as an optical intensity reference. The attery-powered instrument has an on-board microprocessor and digital tape assette for local data processing and data storage.

Report J describes two types of instruments for rapid, sensitive detec of methane gas in LNG vapor clouds developed by the Jet Propulsion Laborato (JPL) for the August-November 1978 LNG spill tests which took place at Chir Lake, California. This report describes the operating characteristics and implementation of a laser instrument with 0.005 second response time and 0.1% sensitivity for methane detection, and a two-band differential radiome

ith this program yielded progress on the development of a modified ent to measure the concentration of oxygen in the vapor cloud, and sis of infrared-transmitting fiber optics for advanced laser detec- ane and other species. The results of this effort are described rt.

K describes the evaluation of instruments used to measure dispersing n four spill experiments at China Lake conducted by LLL. A grab em was developed for use as a reference for other instruments. describes tests on various types of instruments including devices hot wire anemometry, hot catalyst-coated wire and the absorption radiation.

L describes spill tests and instrumentation assessments performed Weapons Center at China Lake. This report covers LNG tests 12 conducted between May 25 and November 20, 1978. The spill ex- elded an extensive amount of data on instrumentation techniques, nbustion and dispersion characteristics, which are still being eport L provides details of the meteorological, photographic, and concentration monitoring instrumentation used in these tests, to examples of radiometer and vapor concentration records.

ffects Experiments

eports in Section III address scale effects experiments. The DOE king a suitable experimental site to investigate the hazards ive potential of large LNG spills. Report M describes the evalu- ned by LLL of potential sites that had been identified in a pre- A list of ten desirable site characteristics was developed, racteristics ordered according to their relative priorities. This d in evaluating the potential sites. It was concluded that the t area of the Nevada Test Site is the most suitable experimental LNG spill investigation.

ment with an extensive spill pond. The criteria discussed are windspeed, lapse rate, atmospheric stability, heat flux, depth of the mixing zone, humidity, fetch, persistence, and turbulence scales. Current studies to characterize Frenchman Flat are mentioned.

Report O documents the results of a study undertaken by PNL to devel and appraise the characteristics and advantages of various experimental strategies for the planned field experiments portion of the DOE LNG Safet and Environmental Control R&D Program. Preliminary experimental strategi and run matrices were developed for studying the following LNG spill phenomena: 1) vapor generation and dispersion, 2) vapor cloud fire (and possible explosion) and 3) pool fire. Both the classical and the statist approach have been considered. Development of the matrices involved the following steps: a) identification of parameters involved in each of the three LNG spill phenomena listed above, b) assessment of the importance o each parameter, c) estimation or selection of a range of values to be ass to each parameter which is assessed to potentially have a first order eff on the LNG phenomena and d) establishment of the experimental matrix of r number and parameter size such that the results of these tests will separ and show the behavior of, the important variables. The assumptions and rationale used in each step are presented.

Report P "Annotated Bibliography: LNG Safety and Environmental Cont Research" is the final LNG-related document in Section III. This report contains references to all aspects of LNG program activity.

I.2.2 Other Liquefied Energy Materials

As indicated above, the preponderance of effort addressing LNG issue in the DOE Safety and Environmental Control Research Program on Liquefied Gaseous Fuels has been motivated by the identification of a need for the

ammonia. Reports Q through T in Section III describe this effort. Summaries of these reports, grouped according to energy material are presented below.

Liquefied Petroleum Gas

Report Q describes initial effort in the LPG assessment performed by subcontractors. This is in support of a DOE objective to assess the safety and environmental control aspects of processing, storing and transporting LPG in the United States. The areas being considered include vapor generation and dispersion, fires, explosions, and release prevention and control. This assessment will include the identification of any areas where additional work may be needed.

The Applied Technology Corporation (ATC) has recently initiated analyses of hazards in the marine transportation of LPG and fire-fighting effectiveness of dry chemicals and high expansion foam. A summary of the work planned and task description of the ATC effort is presented in Report R.

Research on the simultaneous boiling and spreading of LPG on water is being conducted at MIT. This work is reviewed in Report S. Previous boiling and spreading models of cryogenic and noncryogenic liquids spilled on water have been reviewed and all were found to have questionable assumptions. However, the models provide an approximate base upon which to plan experimental tests. A one-dimensional water-filled channel is being constructed to allow measurements of the rate of spread and evaporation for LPG spilled in one end. Gas concentrations, vapor and liquid temperatures, and high-speed movies will be used to quantify the results.

An annotated bibliography is being assembled by ATC to provide data for the LPG hazards analysis task described in Report R. A preliminary version of this bibliography is contained in Report T. This survey is designed to support the estimation of equipment failure rates and frequencies, the

review and assessment of environmental and safety problems in hydrogen energy systems as presented in Report U. The LASL studies on the safety aspects of hydrogen energy systems conclude that the problem of hydrogen embrittlement can be solved through research and that existing regulations and standards are adequate to encompass hydrogen development close to present usage level. Large increases in quantity or degree of public exposure may require reconsideration of existing standards.

It appears that hydrogen gas can be safely transmitted by pipeline. Whether existing natural gas pipelines can be used for hydrogen transmission has not yet been established; however the addition of hydrogen to natural gas in quantities up to about 15% would seem to present no problems.

Hydrogen is commonly shipped as a cryogenic liquid over long distance in unattended rail tank cars or in over-the-road tractor-trailer units. No safety problems have been observed, and this method of shipment could be considerably expanded with existing technology.

Initial investigation indicates that both the production of the neces primary energy and its use in the production of hydrogen may be detrimenta to the environment. However, the generally positive impact of the end-use hydrogen will ameliorate the negative effects of the production process.

Ammonia

Although ammonia is not now used as a fuel, it is a high energy mater handled in international commerce in large quantities. Ammonia is easily assimilated into the environment. Once dispersed, it does not present any significant ecological problems. However, in massive doses it is hazardou to all forms of life. The basic concerns associated with using ammonia ar the safety aspects of production, transportation, storage and use includin

perature; both of these factors are highly detrimental to aquatic

V reviews initial effort at PNL to characterize the properties, azards, production methods, accident statistics, regulations and hniques for ammonia. This will provide a foundation for assessing mental and safety issues and the research and development needs dicated.

of General Relevance

l of the research activities in this program have broader relevance n the basic categories summarized above. The LNG vapor and dispersion model development and comparisons performed by s A and B) provide insight and knowledge potentially applicable quefied gaseous fuels. Report D from MIT addresses the analysis and of radiation resulting from hydrocarbon clouds in general and the g of detonation and deflagration properties (Report E) also applies quefied energy materials. The instrument assessments by JPL, LLL, ports J, K and L respectively) are either directly relevant or extrapolation to other liquefied gaseous materials. Finally, the ies collected both as organized tasks and as research reference each element of program activity provide significant and broadly sources.

REPORT PERSPECTIVE

rpose of this report is to provide a detailed status review of earch addressing issues and needs identified in the DOE's compre- ety and Environmental Control Research Program on Liquefied Gaseous coordinated efforts of many individuals and institutions address ctrum of program activities and requirements contained in the DOE n described in Section II of this report. While ongoing efforts

Reports A through V on the elements of the program undertaken to
To remain topical and preserve the insight of individual authors,
eports are presented without appreciable editing or format standardi-
Collectively they report the substance and current status of the
ctivities in this DOE program.

PLAN FOR

LIQUEFIED GASEOUS FUELS

SAFETY AND ENVIRONMENTAL CONTROL ASSESSMENT PROGRAM

FEBRUARY 1979

U. S. DEPARTMENT OF ENERGY

Office of Assistant Secretary for Environment

Environmental Control Technology Division

Washington, D.C. 20545

ovides that the Administrator of the Energy Research and ministration develop a National Energy Plan and a comprech, development, and demonstration Implementing Program. bilities have been assumed by the Department of Energy (DOE) his program is designed to achieve solutions to short- and gy supply problems, taking into account the economic, environchnological merits of each aspect of potential energy solutions. he National Plan (ERDA 77-1, page 32) has the objective of d characterizing the environmental, health, and safety issues cerns associated with the commercial operation of specific . The Division of Environmental Control Technology has for preparing assessments in some of these areas.

ous fuels are elements of our energy system. Yet these safety and environmental hazards. The purpose of this plan the activities needed to develop, in a timely manner, ety and environmental control information. This information ble for use by industry, regulatory bodies and the general ing decisions about the handling, storage, transportation and nergy materials. This plan describes the major activities tify and develop information.

quid and liquefied energy materials is extensive. As shown e current focus is on Liquefied Natural Gas (LNG), Liquefied (LPG), liquid hydrogen (LH_2), anhydrous liquid ammonia ol and ethanol. Other materials may be considered later. iscussion of the individual materials is not uniform. LNG is he greatest depth because its R&D needs were recently investigated n DOE/EV-0002, "An Approach to Liquefied Natural Gas Safety tal Control Research." LPG is discussed in less depth essment of safety and environmental control research needs is ted.

of Energy is the focal point in Government for assessment and environmental control aspects of handling, storage, , and use of liquefied gaseous fuels. However, a number of es, both within the Department of Energy and other Departments, esponsibilities such that they will draw on the information in this program. These agencies include the Federal Regulatory E), Economic Regulatory Administration (DOE), United States istration (Department of Commerce), United States Coast Guard Transportation, DOT), the Office of Pipeline Safety Regulations Federal Railroad Administration (DOT).

an is consistent with the requirements of the Program and Project ent System for DOE Outlay Programs. Because of the nature of the matter for this plan, several elements required by the Management are merged. Thus one will find <u>risk assessment</u> (Element 3) included <u>ssion needs and objectives</u>. Further, there is no <u>commercialization</u> since the industry is considered to be technologically mature. , there is no <u>environmental annex</u> since the thrust of this whole plan ronmental in nature.

anning document addresses all pertinent safety and environmental issues for liquefied gaseous fuels, but only in a very general Various Annexes, one for each liquefied fuel, to be issued and periodically, will include such specific details as technical schedule, and estimated resource needs. These Annexes will be ive to information gaps identified in preliminary assessments.

TABLE 1

E FOR LIQUEFIED GASEOUS FUELS SAFETY AND ENVIRONMENTAL CONTROL ASSESSMEN

Material	FY 77	78	79	80	81	82	83	84	85
	(1)		(2,3)						
		(1)	(2)	(3)					
ogen		(1)	(2)	(3)					
ia				(1)	(2,3)				
anol/Ethanol					(1)	(2)	(3)		

itiate safety and environmental control assessment needs.
mplete preliminary safety and environmental control assessment.
mplete plan for studies to fill knowledge gaps identified in eliminary assessment.
mplete acquisition of needed information (date depends upon needs d priorities).
mplete final safety and environmental control assessment (about one ar after completion of (4)).

ment of Energy has a responsibility to assess the safety
onmental control aspects of fuels such as LNG, LPG, hydrogen,
ethanol and ethanol to aid in assurance that they are processed,
d, stored and utilized in a safe manner. A safety and environment
ogram to develop an understanding of the effects (hazards,
sequences) of accidents and to identify effective accident
and release control measures should be a high priority item in
ment. Such an effort must provide useful information to support
d future decision making. The program should be sensitive to
erceived by the public and those identified by comprehensive
assessments.

AND OBJECTIVES

f this program is to develop additional safety and environmental
formation for use by industry, regulatory agencies, and the
blic. An early step will be the identification of specific
n needed for the regulatory process or for preparation of
recommendations for legislation. Such specific information
help to more sharply define the research objectives. The information
in this program will aid in making decisions with respect to the
storage, transportation and utilization of these fuels. In particular,
ll to the attention of local, state, and Federal regulatory
ny weaknesses or inadequacies of current safety and environmental
actices for liquefied gaseous fuels. The information will aid
in providing public safety in an economic manner without
edures and regulations that are either overly restrictive or
. It is expected that the dissemination and assimilation of this
n will lead to reduced frequency of accidents and to the mitigation
ences of a mishap should one occur.

ish the program goal, three specific objectives have been identified:

ified Predictive Capability: The development and validation of
lytical modeling capability in sufficient depth to provide firm
hnical foundation for promulgation of regulations and to ade-
tely support the development of prevention and control strategies,
hniques and procedures. Wherever possible, theory and predictive
ability will be based on laboratory experiments. Validation of
dictive capability may require large-scale field tests.

techniques, and strategies which are intended to reduce the impac of a release. By nature, these will tend to be "active" systems.

To assure that, in fact, the specific tasks are addressing the current important issues in an adequate manner, program progress will be continually monitored. Individual technical project reports will be widely disseminated as published. These reports will be subject to peer scrutiny. In addition, periodic critical review of the work and its general direction will be conducted. This review, of both theoretical and experimental results, will assess the implications of the assumptions made about parameters of interest, will weigh the relative significance of the principal variables, and, if necessary, redirect the research tasks or the program.

II.3 SAFETY & ENVIRONMENTAL CONSEQUENCES ISSUES

Energy material properties strongly govern safety and environmental consequences. For energy materials, the very property that makes them fuels (combustibility) is the property that presents a major hazard (fire or explosion). Additionally, the materials may possess other properties which make them hazardous, such as being toxic, water soluble, or a cryogen. A comparison with gasoline of hazards and physical properties is presented for several liquefied energy materials in Table 2. Four of the materials are cryogens, and two (LNG and LH_2) require special cryogenic handling procedures and controls. Three (LNH_3, methanol, ethanol) are miscible with water and therefore require special environmental and safety investigation. Methanol is particularly hazardous since it is both toxic and tasteless.

The potential hazards from all of these fuels must be examined both for land and sea spills. The consequences of a miscible spill on water must be examined. Methods for cleaning up immiscible (e.g., oil) spills are inappropriate for use with ammonia and alcohols. Other counter measures must be considered. Rates of dispersal and reaction of ammonia and alcohol in water must be studied. Biological effects on marine life must be assessed.

Both of the alcohols have the potential for serious poisoning of the local water table. There are certain bacteria which biologically degrade them (e.g., studies have indicated that Psuedomonas fluorescence consumes methanol rapidly and is limited only by nitrogen and phosphorou levels).

n high concentrations. Little is known about the effects of exposure to trace quantities of ammonia, methanol and ethanol.

rison of properties table (Table 2) is displayed in two parts: nd Physical Properties. The flammability limit has to do with over which the given fuel will burn. Thus at a volume percent LNG will not burn and at a volume percent above 15%, LNG will It may be seen that LH_2 possesses the greatest range of ity (4-75%).

ignition temperature is the temperature at which spontaneous n will occur. The flash point is the point at which there is t vapor pressure from the fuel in question to put its vapor ithin the flammability limits. Gasoline is seen to be the act form of energy, followed by LNG.

ROACH

h preliminary assessment will identify and/or confirm information detailed research plan to acquire this information will be prepared. et of elements and tasks are defined for each energy material d. The total list of elements includes:

por generation and dispersion
re and radiation hazards
ame propagation
lease prevention
lease control
strumentation and technique development
ale effects experiments
vironmental and ecological impacts
man health impacts

on the fuel characteristics, part or all of these elements will ed for each energy material. Wherever possible, duplication of ll be eliminated. For example, the results from the generation rsion study of one energy material may also provide a substantial information for another material. For each element, one or more llowing tasks are required: background investigation, analytical

TABLE 2

COMPARISON OF PROPERTIES FOR VARIOUS FUELS

	Liquefied Natural Gas	Liquefied Petroleum Gas	Liquid Hydrogen	Anhydrous Liquid Ammonia	Methanol	Ethanol
A. Hazard Level						
Health						
Inhalation	slight	slight	slight	severe	slight	slight
Ingestion	--	--	--	severe	severe	moderate
Flammability	extreme	extreme	extreme	slight	severe	severe
Chemical Reactivity	none	none	none	severe	slight	slight
Water Solubility	insoluble	insoluble	slight	moderate	moderate	moderate
Flammability Limits						
(in vol. %) Lower	5.	2.2	4.0	16.	6.7	4.3
Upper	15.	9.5	75.	25.	36.	19.
B. Physical Properties(2)						
Flash Point	Gas	Gas	Gas	-	52^oF	55^oF
Boiling Point	-259^oF	-44^oF	-422^oF	-28^oF	147^oF	173^oF
Auto ignition Temp.	1000^oF	874^oF.	1085^oF	1204^oF	876^oF	793^oF
BTU/gal at 68^oF	94,147	87,382	31,802	53,295	59,295	79,111
Research octane number	120	100	-	111	106	106

(1) Gasoline is included for comparative purposes only.

(2) Liquefied natural gas, liquefied petroleum gas, and gasoline are not pure substances, but rather are mixtures. Hence the physical properties can vary somewhat from one sample to the next. The values given for LNG and LPG are, respectively, for pure methane and pure propane, the major constituents of these substances.

ifying models and environmental control systems. The nine
hnical work are elaborated below.

r Generation and Dispersion

tion and vapor dispersion rates and patterns must be deter-
er to assess the possible hazards. Research may be needed to
ions such as:

far from the location of a spill or release can an ignition
he vapors occur?

far can the vapor be toxic?

the vapor cloud be denser than ambient air?

r what circumstances will the vapor cloud become buoyant?

of this element is to provide the needed safety and control
by better defining and quantifying the behavior of materials
ork includes assessment of current knowledge and capabilities,
uct of needed analytical and experimental studies.

and Radiation Hazards

kely hazard associated with the release of the energy materials
eration. Studies in this area are planned to answer questions

far from the surface of a fire is there a burn danger to
ns or property?

credible ignition sources can ignite a vapor cloud?

effect does weather have on the area of hazard?

rts on this topic are directed at providing the needed safety and
rmation relative to fires. Work includes an assessment of
ledge and capabilities and performance of needed analytical and
efforts.

the energy appears predominantly as a mechanical wave with a [illegible] front, whereas in a deflagration the pressure wave is more diffuse and th[illegible] energy is released mainly as heat and light. Flame propagation studies m[illegible] be needed to determine if the detonation hazard is a significant concern. Both the conditions for occurrence and the characteristics will be invest[illegible]

II.4.4 Release Prevention

Studies in this area may be needed to provide an answer to how accidental releases of fuels can best be prevented. This work may investigate modif[illegible] tions to the materials under consideration, the techniques by which they are handled, or the operating procedures of various types of facilities.

II.4.5 Release Control

Studies in this area may be directed to provide methods of controlling routine and accidental releases of fuel materials. Cryogenic effects might pose special release control problems. This may include equipment and procedures to collect the material or render it harmless.

II.4.6 Instrumentation and Technique Development

The purpose of this element is to develop adequate instrumentation desig[illegible] measurement techniques to obtain high quality data from experimental stu[illegible] This work will include the determination of instrumentation requirements and the development and testing of new instrumentation where current equ[illegible] ment does not meet the performance specifications.

II.4.7 Scale Effects Experiments

This element is directed at providing the experimental data necessary to firmly establish analytical models which can predict the effects of larg[illegible] scale events (release, fires, etc.). To date, research has involved releases of relatively small amounts of material, orders of magnitude smaller than those that may be stored or shipped in a single tank. Vari[illegible] consequence prediction models have been developed and tested against dat[illegible] from these smaller spills. The crucial question is whether or not such models are adequate for extrapolation to spills thousands of times large[illegible] i.e., how do the model parameters scale with spill size? Because of the importance of this question and the relatively large commitment of resources that will be necessary to answer it, the scale effects experimental work is considered as a separate element.

t. The purpose of this element is to provide the needed trol information by defining environmental pathways and ecies that are likely to be impacted by an accidental spill.

Health Impacts

lls may cause humans to be exposed to high concentrations of s. Further study may be needed to determine the exposure, doses The purpose of this element is to provide the needed safety and ation by defining the specific impacts of the energy materials.

ATION

ll be coordinated within DOE and with other Federal agencies rest and responsibilities in these commodities. Specifically, are:

partment of Transportation

Coast Guard
ce of Pipeline Safety Regulations
ral Railroad Administration

partment of Commerce

time Administration
onal Bureau of Standards

ll be coordinated with various industries (e.g., Gas Research sts may be shared with them. Recommendations from industrial rial organizations will be received and considered.

ES

gram (for all liquefied gaseous fuels) will almost certainly ation of a suitable site at which to conduct scale-effects Preparation of a suitable site for safely conducting these estimated at this time to require about \$15 to \$25 million. ds of perhaps \$5 to \$15 million will be needed for each fuel rry out the field experiments, to perform the supporting laboratory work, and to integrate the new knowledge with

later, will have a legacy of initial information on which to build and will probably be less costly.

The current and proposed budgets for this program are shown in Table The projected budget needs for LNG, LPG, and liquid hydrogen depend u final program planning and review. The budget needs for ammonia, met and ethanol will be determined at a later date.

II.7 PROCUREMENT STRATEGY

It is anticipated that any required field site for conducting scale e experiments will be on Government-owned property. It is likely that national laboratory will be the overall program manager for the porti the program concerned with field tests. Other tasks which are identi in this plan or as a result of carrying out this plan may be contract through, for example, RFP's or unsolicited proposals. There are a va of profit and not-for-profit organizations, including the DOE nationa laboratories, with the talent, interest, and background needed to per research in this area.

TABLE 3

LIQUEFIED GASEOUS FUELS SAFETY AND ENVIRONMENTAL CONTROL ASSESSMENT BUDGET
(Dollars in thousands)

Energy Material	FY 76	77	78	79	80	81	82	83	84	85
LNG	200	900	2300	2200*	6680*	**				
LPG	-	40	90	470*	810*	**				
Hydrogen	-	150	150	150*	100*	**				
Ammonia	-	-	-	-	300*	**				
Methanol/ethanol	-	-	-	-	-	**				
TOTAL	200	1090	2540	2820*	7890*	**				

* Projected budget needs pending final program planning and review
** Schedule and budget for future years depend, for each fuel, upon the conclusions reached in the safety assessment, *the progress in research on technical tasks, and the* priority accorded the program.

This section presents an overview of that portion of [cut off] program specific to LNG. Details of the LNG safety research program will be found in Annex A, to be published in late FY 1979.

III.1 PRESENT AND FUTURE SUPPLY AND USAGE

Currently about 28% (approximately 13.6 Tcf) of United States energy comes from natural gas. The United States natural gas reserves are limi[ted] and there have been recent regional shortages of natural gas due to limi[ta]tions of the supply and distribution systems.

Increased importation of natural gas may assist in the near-term solutio[n] of the supply problem. Increased storage of natural gas at critical regional locations in the distribution system will aid in the solution o[f] the distribution problem in seasonal periods of high demand. Natural ga[s] can be transported and stored in the liquefied form rather than the gaseous form with the specific advantage of a factor of 600 volume reduc[-]tion associated with the liquefaction process.

In 1977, LNG imports provided an estimated 10 billion cubic feet (Bcf) o[f] natural gas; this is less than 0.08% of the annual gas consumption in th[e] United States. It has been projected that such imports could increase t[o] 2.8 trillion cubic feet (Tcf) of natural gas annually, which would be approximately 10% of the annual gas consumption in the mid-1980s. Compa[red] to the transportation of noncryogenic fuels, the transportation of LNG i[s] relatively new technology; however, as an indication of the current use [of] LNG elsewhere in the world, imported LNG provides almost 80% (approximat[ely] 0.35 Tcf natural gas) of Japan's total annual gas supply.

III.2 SAFETY AND ENVIRONMENTAL CONTROL ISSUES

There is a perception by some that current and planned LNG operations an[d] facilities present an unacceptable risk to the public. This perception may work to limit the number or capacity of LNG facilities at a time whe[n] the dependency of certain regions upon natural gas might be met by increased usage of LNG. Attention has focused on the limited amount of meaningful data on which sound judgments could be made. Accordingly, regulatory bodies at all levels of Government may be handicapped in cond[ucting] the analyses needed in reviewing license applications.

ty record in the transport, transfer, processing and storage of ood. The need for this program arises from a projected change in size and characteristics in the United States and from the absence led knowledge needed to evaluate risks and consequences. Another his program is needed is the potentially high cost to the consumer rectly designing safety features.

rtation of liquefied natural gas, by supplementing domestic of natural gas, can aid in the solution of the natural gas shortage. ected future demand for LNG, combined with the current differences on on the hazards involved, strongly supports the need for an ed LNG safety and environmental control program of the type d here.

ROPOSED PROGRAM GOALS AND OBJECTIVES

ose of the integrated LNG safety and environmental control program ovide additional LNG safety and control information for use by , regulatory agencies and the general public. This information disseminated periodically through a variety of methods (e.g., l publications, symposia, annual reviews) to permit earliest and ossible utilization. In particular, the information must be pertinent egulatory process.

stinct objectives have been established: verified predictive ty, verified prevention methods, and verified control methods. To se objectives, work will be undertaken in seven technical areas: neration and dispersion, fire and radiation hazards, flame propagation, prevention, release control, instrumentation and technique development, e effects experiments.

and environmental control ...
an LNG program plan began in the late fall 1976, building on information developed in a cooperative program with the U.S. Coast Guard and the American Gas Association and from review of reports of the numerous past LNG safety and control studies. Further input came from an LNG Safety and Control Workshop held in December 1976, which was attended by over 40 persons selected to represent a cross-section of regulatory agencies, industry, research organizations, and others familiar with the current status, technology, and issues of LNG safety and control. The purpose of the Workshop was to develop, to the extent possible, a consen on research priorities for the most visible of these questions. Followi analysis and evaluation of all of the various inputs, work on preparatio of a comprehensive plan was initiated.

The plan was prepared in light of the acute current need for information about the effects, the control, and the prevention of LNG spills, from both a public safety and an operational safety point of view. It is expected that additional viewpoints will be advanced through the program and they will be given appropriate consideration based on technical meri An integrated approach will achieve the maximum meaningful results in th minimum time with the limited available resources of funds, facilities, qualified personnel, and supply of LNG for experiments.

The main question which regulatory bodies must address is that of siting For a particular site, what are the impacts that may be expected on persons and property proximate to the plant in the event of an accidenta release? Specifically, what are likely to be the hazards from heat, fir explosion, toxic fumes, etc., released as a consequence of an accident a an energy storage or transfer facility? In order to decide whether adeq controls exist (e.g., sufficient distance between plant and public, prop construction materials, response strategies) for a given site and a seri of alternate sites, quality scientific data whose validity is accepted m be available to the regulators.

Work is proposed in seven technical areas. For each of these, the types of questions which the work is designed to answer are given.

tioned later.)

ludes an indepth assessment of the limitations of current and conduct of the additional experimental and tudies identified as necessary by the assessment.

stions which this element is designed to answer are:

is the geographical extent and local composition of a vapor d as a function of pertinent variables, such as spill , spill rate, and wind speed?

does the vapor generation rate depend upon the properties ne substrate surface, such as type of material, porosity, hness, and heat conductivity?

gram Element - Fire and Radiation Hazard

e of this element is to develop an adequate validated o predict the characteristics of pool fires from LNG ven, for example, release size, weather conditions, operties, and characteristics of ignition sources. The s an indepth assessment of the limitations of current and conduct of the identified additional experiments and tudies necessary to achieve the objective.

questions which will be answered by this element are:

hat distance from a pool fire will the radiation be harmful umans? To property?

is the effect of atmospheric conditions on the extent of thermal hazard zone?

gram Element - Flame Propagation

e of this task is to develop an adequate validated capability he characteristics of various aspects of vapor cloud deflagration detonation and of flameless (nonchemical) reaction of LNG upon water. This task includes the so-called "fireball" event, in ixed vapor cloud combusts nearly simultaneously in all its parts, emitting radiation at rates significantly higher than normal.

- o What factors affect the speed at which a flame travels through vapor cloud?

- o What will be the effect on flame speed of pockets rich or lean

- o Under what circumstances, if any, will a burning cloud evolve t detonation?

- o Will a "flameless" explosion have impact only locally or global the vapor cloud?

III.4.4 Program Element - Release Prevention

The objective of this element is to develop an adequate understanding c the processes, phenomena and other factors that could defeat release prevention systems and their regulations.

The work in this task will encompass those features of LNG facility des equipment design, and operation of importance in release prevention.

Typical questions which this element is designed to answer are:

- o For a given generic facility, by what mode are releases most li to occur?

- o What options of design or operating procedure are possible to d the likelihood of such a release?

III.4.5 Program Element - Release Control

The objective of this element is to develop an adequate understanding o the processes, phenomena and other factors that could defeat release control systems and their regulation.

The work in this task will encompass those features of LNG facility and equipment design and operation of importance in release prevention.

Typical questions which this element is designed to answer are:

- o For a given generic facility, what techniques or strategies would be most fruitful in responding to a release and controllin it?

are inadequate.

will include the determination of instrumentation (e.g., senors, onditioning equipment) required to carry out experimental work program, setting performance specifications, and development and of new instrumentation where current equipment does not meet the nce specifications.

questions which this element is designed to answer are:

re available instruments adequate for the support of the research o be done?

re we able to conduct the field experiments in such a manner that ne maximum useful information will be obtained for the given esources?

Program Element - Scale Effects Experiments

ctive of this element is to conduct scale effects experiments, if . The experiments will involve LNG spills on both land and water, to establish scaling factors for the results of small-scale experid to confirm the accuracy of improved mathematical safety models and ormance of control provisions to an acceptable level.

may include conducting experiments to investigate vapor on and dispersion, fires, and flame propagation. These nts will be of various sizes and will require experimental t design, site preparation, experiment planning, performance of riments, data reduction, and analysis of the results. Ancillary related to spill prevention and control are also planned. l be conducted using some of the storage and processing t that will support the spill experiments.

questions which this element is designed to answer are:

ow do the hazards vary with spill size?

ow do the hazards vary with spill rate?

ow do the hazards vary with weather conditions?

re control schemes which look promising, based on smaller experiments, till useful for larger spills.

The planning effort for Liquefied Petroleum Gas (LPG) was initiated in June 1978. This Chapter outlines status and nature of this work. Details will be presented in Annex B, expected to be published in mid FY 1980.

IV.1 PRESENT AND FUTURE SUPPLY AND USAGE

Liquefied petroleum gas includes propane, butane, and various propane-butane mixtures, including small amounts of other hydrocarbons which may be present naturally. The supply of these materials is shown in Table 4. Since about 75% of the LPG comes from natural gas sources, its production is very closely related to natural gas production. The remainder comes from liquefied refinery gases. The Gas Processors Association (GPA) expects a growing deficit between demand and domesti production with a resulting growth in LPG imports. Therefore, the exp growth in the LPG industry will probably be in large volume transporta and storage facilities. The GPA reports that underground storage faci for light hydrocarbons have been increasing at about 8% per year and reached an estimated capacity of 375 million barrels at the end of 197

IV.2 SAFETY AND ENVIRONMENTAL CONTROL ISSUES

Because accidents involving LPG have occurred, concerns have been expressed by DOE and by a part of the Congress on the adequacy of safety and environmental control provisions and regulations applicable to LPG. One need in responding to this concern is to examine the technological bases for such provisions and regulations and determine what, if anything, should be done to assure industry, Government and public of the soundness and adequacy of these bases.

The LPG industry utilizes two basic methods of maintaining the material in a liquid state. During transport and storage some systems are pressurized to maintain the boiling point at or above ambient temperature. Other instances utilize refrigeration processes to condense the gas and keep it in a liquid state at or near atmospheric pressure. This temperature is about -40°F for some of the common materials.

	(Est.) 1973	1974	1975	1976	1977	(Projected) 1978
Propane	213	207	201	190	185	181
Other LP-Gas	126	123	120	114	111	107
Liquefied Refinery Gas (LPG)	137	122	114	120	125	126
TOTAL DOMESTIC	476	452	435	424	411	414
LPG Imports	48	45	41	47	75	
TOTAL SUPPLY	524	497	476	471	486	

ation work (if any) for, safety and environmental
n processing, storing, transferring and transporting
petroleum gas in the United States.

will include identifying the overall scope of the LPG industry, sting and anticipated, from production to utilization. Port s, major storage facilities (e.g., peakshaving plants), water , truck transport, rail transport, and pipelines will be l as to numbers, locations, process variations and general in use and contemplated. A general description of intermediate smaller installations and containers utilized by wholesale retailers, industrial users, and domestic consumers will also ded.

current studies of LPG properties, release prevention and vapor generation and dispersion, fires and explosions will be ed and assessed. This preliminary assessment will define those ere additional information is needed to assure that an adequate e base is available for establishing standards, specifications lations for safety and environmental control issues in the LPG .

OPOSED PROGRAM ELEMENTS AND TASKS

ticipated that the necessary elements and tasks may closely hose required for LNG. However, they will be included as a of the LPG Preliminary Assessment scheduled for completion in 980.

ompleted in FY 1979. This chapter outlines the work as perceived. Details will be presented in Annex C, expected lished in mid FY 1980.

ENT AND FUTURE SUPPLY AND USAGE

d "hydrogen economy" has been an interesting subject for a years. However, it probably won't move toward realization present supplies of fossil fuels dwindle. The largest current drogen is for the production of ammonia and in hydrodesulfurization racking operations in refineries. Currently the most economical hydrogen is the steam reforming of methane or natural gas. The supply of these sources is uncertain. Hence, if hydrogen is to ous competitor as an energy material, it seems that some source such as water must be used. Electrolysis is the only ed method of obtaining hydrogen from water at the present, but nical splitting of water may become promising for the future.

glamorous use of hydrogen today is in space flight. The National cs and Space Administration consumed an estimated 23 million hydrogen in 1978. In the 1980's, when the space shuttle operation, the annual demand for this use could be about 20 ounds. Aircraft makers are also looking into using hydrogen quid hydrogen is expected to permit smaller wings, larger and reduced gross weights. The engines would be quieter and duce less pollution (very low NO_x).

as some basic advantages over hydrocarbon fuels. Its high nsity makes it a desirable form for transporting and storing iquid hydrogen pipeline transmission is, for example, more l than electric transmission by high voltage lines. Also, s much more easily stored than electricity, something that e it easier to meet fluctuating demand.

CY AND ENVIRONMENTAL CONTROL ISSUES

very little experience with liquid hydrogen spills except for s conducted in the early 1960's. These tests confirmed the e concerned about flammability and the fireball phenomenon. no indication that hydrogen would be a serious problem in the nt nor that it is physiological active. High concentrations

to be more prominent than cryogenic burn.

V.3 PROPOSED PROGRAM ELEMENTS AND TASKS

These will be determined as a part of the hydrogen assessment now underway. A preliminary draft report is due at the end of FY 1979.

ent work on ammonia will be initiated in FY 1980. A preliminary report will be prepared in FY 1979 to support this planning is chapter outlines the ammonia project as presently perceived. l be presented in Annex D, expected to be published in late

NT AND FUTURE SUPPLY AND USAGE

not presently in wide use as a fuel. However, it is considered le substitute for hydrocarbons and the U.S. Army has conducted tests in conjunction with its "Energy Depot" concept (1965) where ht be produced and used under field conditions. Ammonia has roposed as an intermediary form by which natural gas energy ansported from arctic regions. Another suggested use of ammonia orking fluid in OTEC (Ocean Thermal Energy Conversion) systems. e largest present use of ammonia is as a fertilizer. In 1976, n metric tons of synthetic anhydrous ammonia were produced ed States. Approximately 80% of this ammonia was used as a direct fertilizer and in the production of other fertilizer products such monium nitrate and ammonium phosphates. The remaining ammonia manufacture non-fertilizer materials such as ammonium nitrate ves, urea for animal feeds and resins, nitric acid, acrylonitrile amines.

produced in 30 states by 90 plants. These plants are located Texas, Louisiana, California and the Central Plains states. is the feedstock for 98% of the synthetic production of mmonia. If natural gas supplies are limited or too expensive, possible to use oil and coal in the production of ammonia. e problems of gasification and purification associated with these ake them undesirable as long as natural gas is available.

mmonia may be handled as a gas under pressure or as a cryogenic ling point $-33^{\circ}C$ at 1 atmosphere). Ammonia is shipped in , rail cars, barges, pipelines, and tankers. Anhydrous ammonia of international trade; in mid-1978, vessels of 75 thousand s capacity unloaded ammonia from Russia at Tampa, Florida, and xas. The cyclic demand pattern for ammonia makes it necessary e storage vessels. Pressurized and refrigerated storage tanks r this purpose.

evere attack of the sensitive membranes of the eyes, nose, throat nd lungs, depending on the concentration. Because of its great ffinity for water, it is particularly irritating to moist skin urfaces. Concentrations cause in the range of hundreds of parts per illion serious coughing, bronchial spasms, and asphyxia; higher oncentrations cause certain death.

ome relevant questions which can be asked about the consequences of an ccidental spill of ammonia from a pressurized container are:

- How far will a vapor cloud extend? Where is the toxic limit? Where is the irritant limit?
- How will the cloud disperse? What are the effects of atmospheric moisture, wind velocity and stability?
- How fast will the vapor cloud disperse? What factors significantly speed up or slow down this process?

n the event of a spill from a cryogenic container:

- What is the extent of the hazardous zone from cryogenic burns?
- How long does the cryogenic danger last?

mmonia is highly soluble in water, with a large heat of hydration. ence any spills of ammonia will also quickly impact the aqueous parts of he surrounding ecosystem. Some relevant questions which may be asked are:

- What fraction of the ammonia is taken up by the water?
- What are the immediate and long-term effects? Which species are most likely to be affected?
- Over what distance is the lake or stream affected by the ammonia?
- What sorts of control measure are effective?

I.3 PROPOSED PROGRAM ELEMENTS AND TASKS

hese will be determined as a main part of the FY 1980 work.

...ll be presented in Annex E, expected to be published in

...SENT AND FUTURE SUPPLY AND USAGE

...nol and ethanol have been used as automotive fuels on a trial ...e very first cars burned pure methanol. It was not until almost ...gasoline was used exclusively. In its pure form, methanol has ...uel of choice in racecars for a long time. Both methanol and ...e high octane fuel; they have research octane numbers (RON) of ... blending RON of from 116 to 156. The majority of studies have ...% by volume mixture of either methanol or ethanol in gasoline. ...ul 2-million-mile test was conducted in Nebraska using ... 10% by volume mixture of ethanol and unleaded gasoline. ...red with unleaded gasoline, analysis of this test showed no ...fects with the GASOHOL and a 6% increase in mileage.

...oduction of methanol and ethanol is inadequate to meet present ...energy requirements. Additional facilities would be needed if ...s were used as energy sources.

...also called methyl alcohol, wood alcohol or carbinol) may be ...structive distillation of wood or by catalytic synthesis from ...oxide and hydrogen. Annual production in 1971 was 5.01 billion ...49,423 barrels per day. Methanol is primarily used to manufacture ...de. Methanol is used as a solvent for various fats, oils, and ... is used for methylation of organic compounds; and is used as a ...cecars and in antifreeze solutions.

...lso called ethyl alcohol, grain alcohol, or methyl carbinol) is ...y the fermentation of sugar solutions and saccharified mashes ...containing materials or synthetically from ethylene. Most ethanol ...ade synthetically from natural gas. Ethanol is used as a solvent ...rs, varnishes, explosives, rubbers and antiseptics; is used as ...eze solution; is a building block for chemicals; and has miscel...plications as a preservative and antiseptic. The total production ...ic ethanol in 1971 was 1.96 billion pounds or 19,387 barrels per day.

...ETY AND ENVIRONMENTAL CONTROL ISSUES

...s more toxic than ethanol. Methanol possesses distinctive ...roperties. Once absorbed, methanol is only very slightly eliminated. ...s considered to be a cumulative poison. Severe exposure may cause

Methanol is easily produced from natural gas. Since this is an energy efficient form for transportation, a prime source for large quantities of methanol could be the Middle East. It is thus anticipated that larg volumes of these chemicals will be shipped by tanker. The probability of an ocean spill is thus very real. This poses very serious environmental consequences. Both methanol and ethanol are completely miscibl with water. Alcohol spills could not be cleaned up by the same technic as oil spills.

A preliminary literature review indicates that short-chain alcohols are, in general, quite toxic to aquatic organisms and homeothermic animals. Few, if any, studies are available on the effect of alcohols on the aquatic ecosystem. This is an area which requires investigatio to determine the actual effects of both methanol and ethanol on aquatic organisms. The dispersion rate of an aquatic spill must be determined.

Methanol cannot be detected in water by taste until it reaches a concentration which is ten times greater than the maximum safe level. Of special concern will thus be to insure the safety of any underground storage. Slight seepage could result in severe pollution of groundwaters.

VII.3 PROPOSED PROGRAM ELEMENTS AND TASKS

These are to be finalized in the FY 1981 work.

Boil-Off for a Spill of Liquefied Natural Gas on a Water Surface

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FIGURES

tuents. A listing of the computer code, LNGVG, developed for these calculations is included. This code can be used to ate effects for instantaneous, continuous or finite duration uous spills. Calculations for two spill experiments conducted na Lake have been made and are compared to the experimental data.

ion.

G is composed primarily of methane with small fractions of ethane pane. These constituents have different heats of vaporization ling points with the result that they boil off at different rates. fferential boil-off during vapor generation results in LNG vapors ing different fractions of constituents than the originally spilled

computer program called LNGVG to calculate LNG Vapor Generation ferential boil off has been written. Using this code, calculations radius, differential boil-off, spreading rate and pool break-up made for instantaneous, continuous, and finite duration continuous of LNG on water. Using this code, two calculations have been made dict the boil off of each constituent of LNG for two spill tests ted at China Lake.[1] A listing of this code is given in Appendix A.

SION

he calculations for the spreading of LNG are approached by determin- e velocity of the leading edge of the LNG pool. This velocity is ined by considering the outer edge as a density intrusion. The radius pool as a function of time is determined from the velocity equation. ool break-up is assumed to occur after spilling has stopped and when ickness of the LNG reaches an experimentally determined minimum thicknes

lly and given as a regression rate (i.e., cm./min.). This rate represents the sum of the contributions from each of the uents. The fraction of this regression rate applicable to each tituents is determined in the calculations by the relative of their heats of vaporization, boiling temperature and volume This relative fraction of total boil-off for each constituent time and is different from the original volume fraction of the LNG

CENARIO

enomena that occur during a continuous spill of finite duration ed below. The LNG is assumed to be spilled at a constant rate e time.

nitially the LNG spreads radially at a rapid rate, which decreases s the radius increases. Boil-off of the LNG takes place as soon s the LNG contacts the water surface. Due to the differential oil-off phenomenon, the vapors generated have different volume fractions than the initial LNG. Also, the volume fraction of the NG constituents of the LNG on the water surface changes due to he differential boil-off.

he LNG spreads out to a radius large enough to vaporize an amount f LNG equal to the rate of LNG spill. The composition of the NG spilled on the water surface continues to change due to differential boil-off until a condition is reached where the rate of

...olume fractions different from the original LNG volume fractions.

(4) The volume of LNG left on the water decreases as vapor generati... takes place until the pool begins to break up in the center. Initially just a small circular area of water is visible. This circular area increases with time until the entire mass of LNG has evaporated.

...ICAL RELATIONS

...ius of the LNG spilled on the water surface is given by equation(1)

$$r = 1.35 \left(g \frac{\rho_w - \rho_{LNG}}{\rho_w}\right)^{1/4} V^{1/4} t^{1/2}$$

r = radius

ρ = density of LNG or water (w)

V = volume of LNG on water surface

t = time

...velocity of the leading edge of the LNG is given by differentiating ...2) with respect to time while holding V constant:

$$\left(\frac{dr}{dt}\right)_{V=\text{constant}} = \frac{1.35}{2} \left[g \frac{\rho_w - \rho_{LNG}}{\rho_w} \right]^{1/4} V^{1/4} t^{-1/2}$$

successive time intervals, Δt, is given by:

$$= r_N + \left(\frac{dr}{dt}\right)_{V=V_N} \Delta t$$

V_N is given by:[3]

$$V_{N-1} + [\dot{V} - EV_{N-1}] \Delta t$$

rate of addition of LNG

Rate of evaporation of LNG

a continuous LNG spill, the maximum radius of the pool is

$$\pi R^2 K$$

maximum pool radius

LNG regression rate (length/time)

lage of the LNG has stopped, the maximum radius, R, attained assumed to remain constant. During this condition, evaporation til the average LNG pool thickness, h, equals 0.183 cm.[2] and break-up occurs. Pool break-up initially occurs at the center

...ak up results in pool break-up occurring sooner.

Also experimentally obtained is the rate of LNG boil-off expressed a... ...ession rate in units of, for example, cm. of LNG per second. A value ... 0.0423 cm. per second[5] was used in the subsequent China Lake calcul... ... rate represents the sum of the regression rates for each of the vari... ...tituents of the LNG. The regression rate for any individual constitu... ...alculated as follows with I = 1 corresponding to methane (CH_4):

$$K = \sum_I \frac{(C_p \Delta T + HVAP)_{CH_4} \, \rho_{CH_4} \, FRI(I) \, A}{(C_p \Delta T + HVAP)_I \, \rho_I} = \sum_I K_I \, FRI\,(I)$$

...e K = experimentally determined LNG regression rate

C_p = specific heat

ΔT = number of degrees that the boiling temperature of constituent I is above the initial LNG boiling temperature.

HVAP = heat of vaporization

ρ_I = liquid density of constituent I

FRI(I) = volume fraction of constituent I in the original LNG

A = unknown regression rate to be solved for.

...lving (6) for "A" and plugging into the below equation (7) gives the ...ion rate, K_I, of constituent I:

$$K_I = \frac{(C_p \Delta T + HVAP)_{CH_4} \, \rho_{CH_4} \, A}{(C_p \Delta T + HVAP)_I \, \rho_I}$$

...uent in the spilled LNG. Addition of constituents to the spilled
...mined from the rate of spill and the known volume fractions of the
...f constituents from the spilled LNG is by evaporation. The amount
...n a time step Δt of constituent I is given by ΔV_I:

$$= K_I F S \Delta t$$

= volume fraction of constituent I in the LNG pool

= surface area covered by LNG pool

...ations, the mixture of the constituents is always assumed to
...s.

...e relations have been incorporated into a computer code called
...ting is provided in Appendix A. Use of this code involves
... input file called LNGIN which contains the information called
...ad statements 6 and 8. Input variables and their units are
...the comment cards at the beginning of the code. Output is all
...an output file called LNGOUT.

...ions for two anticipated spills at China Lake have been made.
...nditions for each spill are given below:

...mber	:	LNG 18	LNG 19
...f LNG spilled (m^3)	=	4.4	4.0
...LNG spillage (m^3/min)	=	4.0	4.0

LNG Regression Rate (cm/sec)		[illegible]	
Water Density (kg/m^3)	=	1,000	1,000
Initial LNG Density (kg/m^3)	=	439	439
Wind Speed (m/sec)	=	10	2

RESULTS

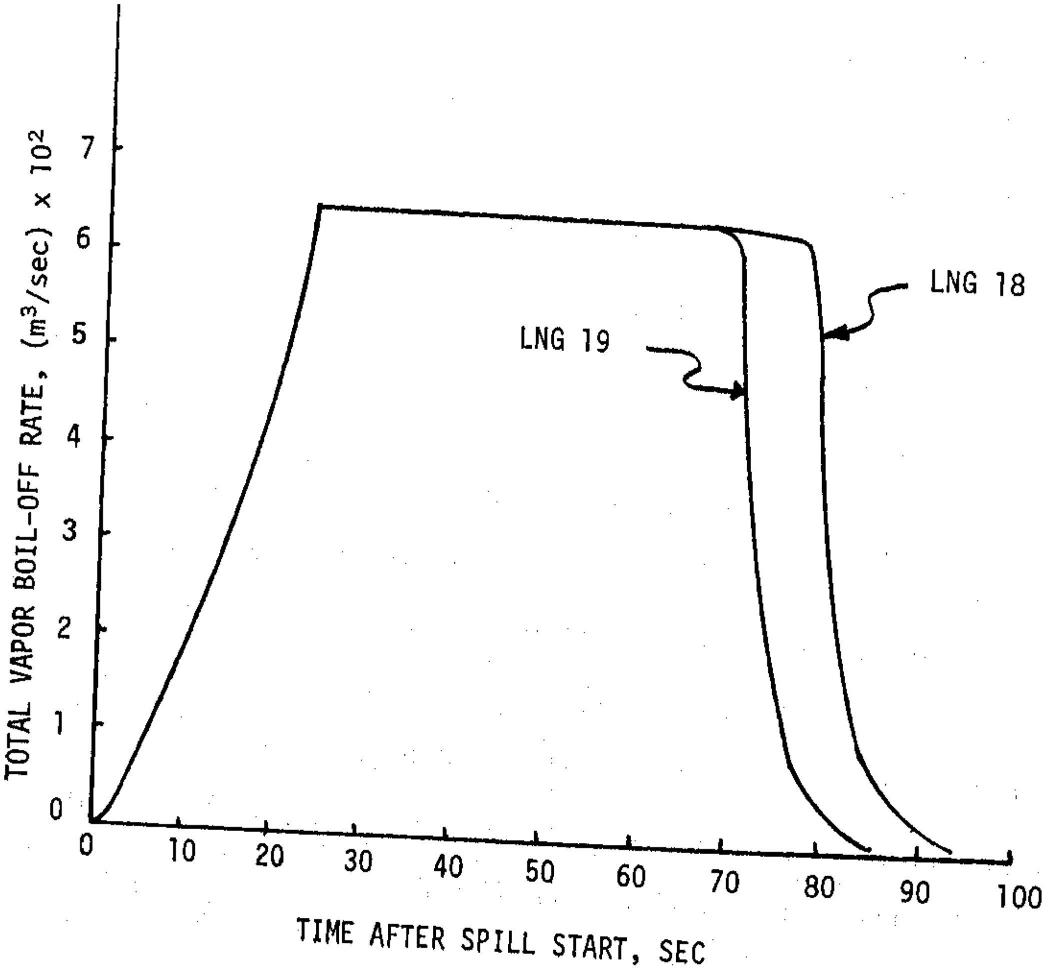
The results of the calculations for the volume fraction of each constituent in the vapors generated vs. time is shown in Figures 2 to for test LNG 18 and in Figures 5 to 7 for test LNG 19. From these figures, one sees that the initial volume fraction of methane in the vapors is greater than the original fractions in the LNG, and the initial volume fractions of ethane and propane are less than the original LNG. The volume fractions in the vapor adjust themselves with time, however, until at the end of spilling, the vapo have approximately the same volume fraction as the original LNG. Aft spilling stops, the volume fraction of methane decreases and that of ethane and propane increases continuously until all the L has evaporated.

The maximum radius attained by the LNG pool in each test is 23 f a time of 23 seconds. Pool break-up is calculated to occur after 77 seconds for tests LNG 18 and 19 respectively.

The total boil-off rate (m^3/sec) vs. time for each spill is sho on Figure 1.

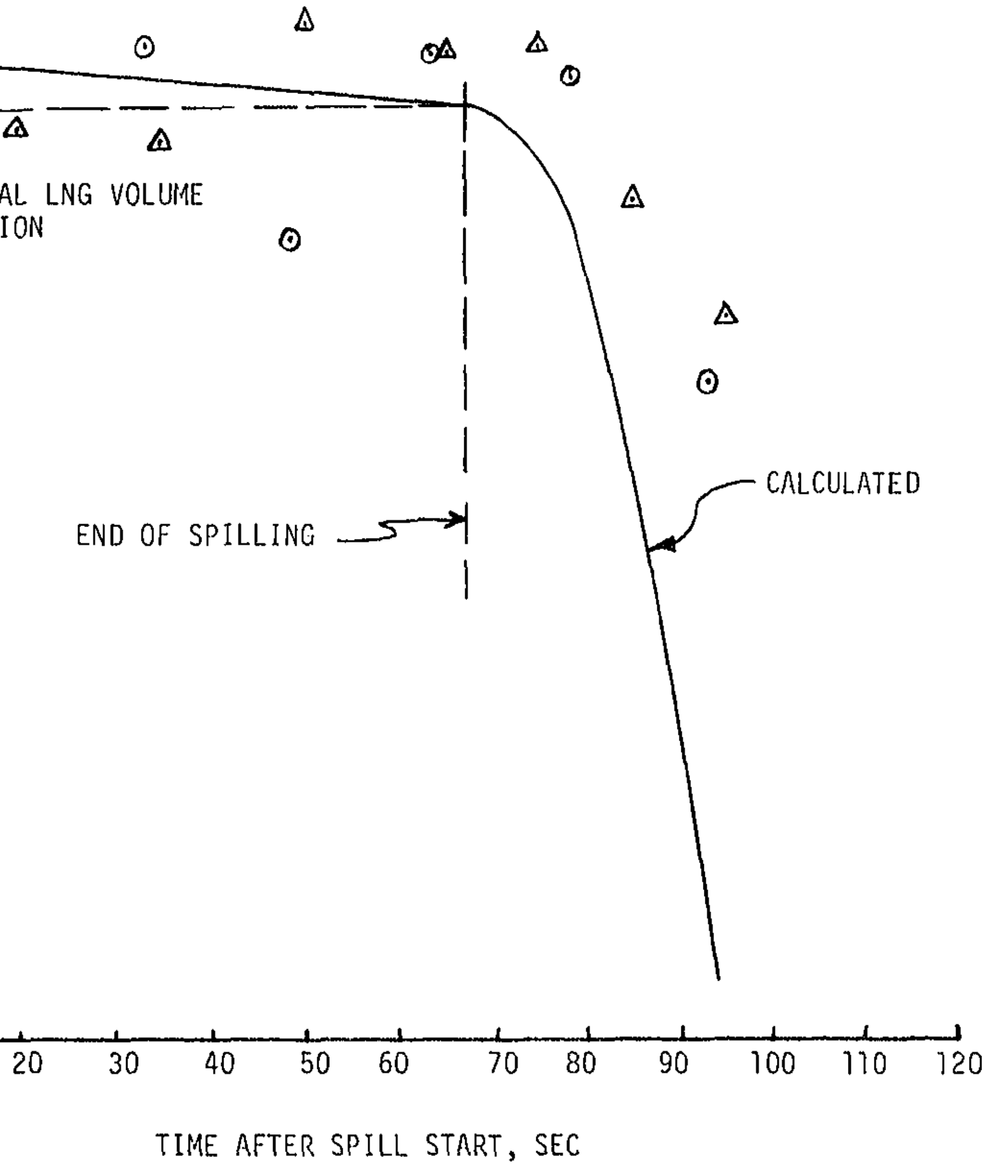
boil-off data. The data is shown in Figures 2 to 7. The
ined in each test from a measurement station, with station
ed 25 and 50 feet respectively from the spill center. The
favorably with the calculations. The calculated curves
slightly to the left of the experimental data points. This
ue to the fact that the LNG spilling from the spill pipe
abruptly upon valve closing, but rather continues to spill
easing rate until the spill pipe is emptied. The calculations
p change in starting and stopping the LNG spilling. If this
ccount in the model, then the data points and calculated
pected to essentially coincide at times after spilling stops.
to weathering of the LNG in the spill tanks, it is suspected
is not homogeneous but during initial spilling is weathered
e. In the spill tests only one sample of the LNG was taken,
uture experiments numerous samples will be taken.

ons with other models[5,6] have been made for instantaneous
on water and the results are tabulated in Table I. The
volves maximum time to evaporate and maximum pool radius
eous spills of 10 m^3 and 1000 m^3. The calculated results
e models agree rather well.

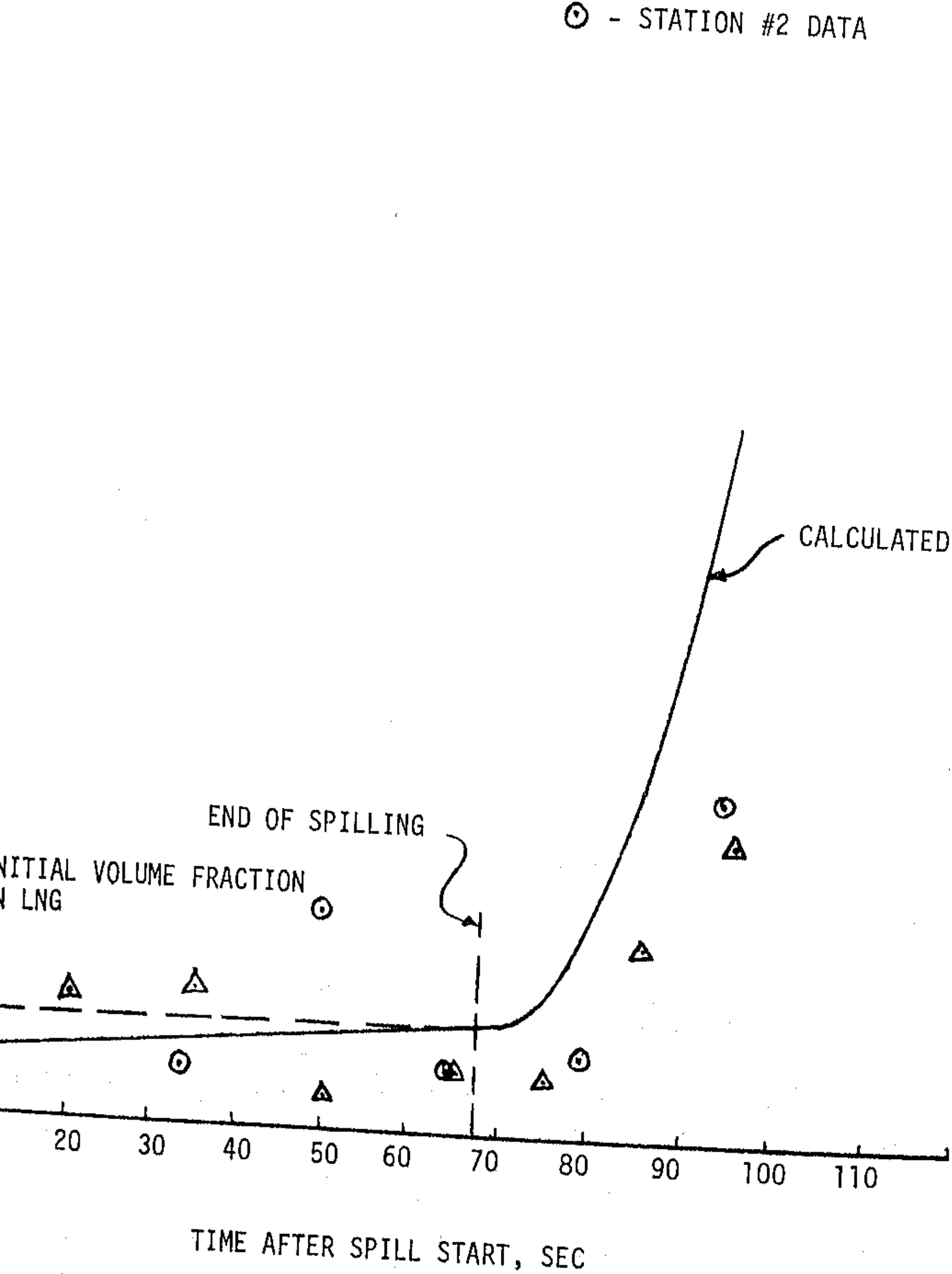


TOTAL VAPOR BOIL-OFF RATE, (m^3/sec) x 10^2
7
6
5
4
3
2
1
0
LNG 19
LNG 18
0
10
20
30
40
50
60
70
80
90
100
TIME AFTER SPILL START, SEC

FIGURE 1

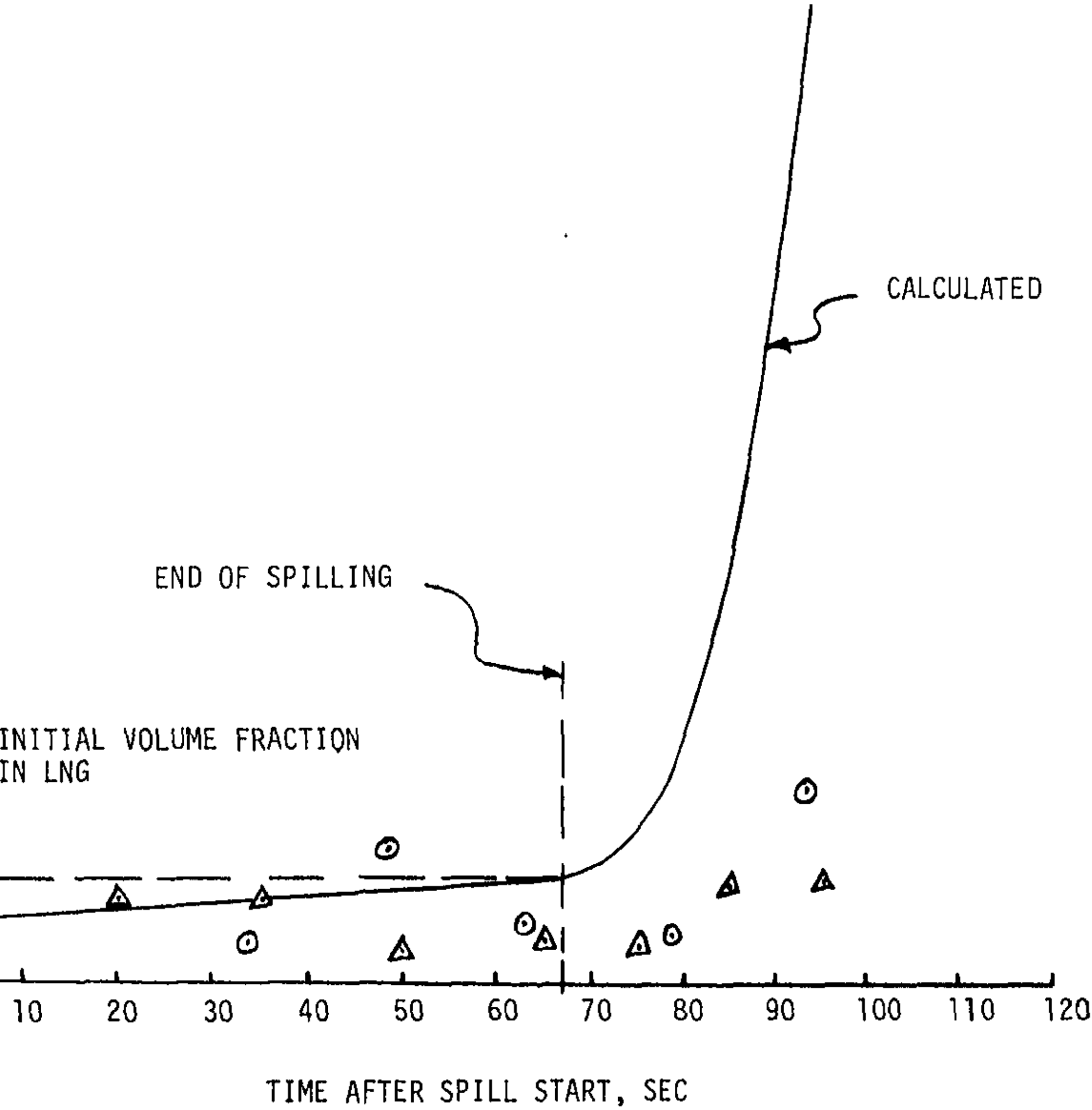

AL LNG VOLUME
ION
END OF SPILLING
CALCULATED
20
30
40
50
60
70
80
90
100
110
120
TIME AFTER SPILL START, SEC

F I G U R E   2



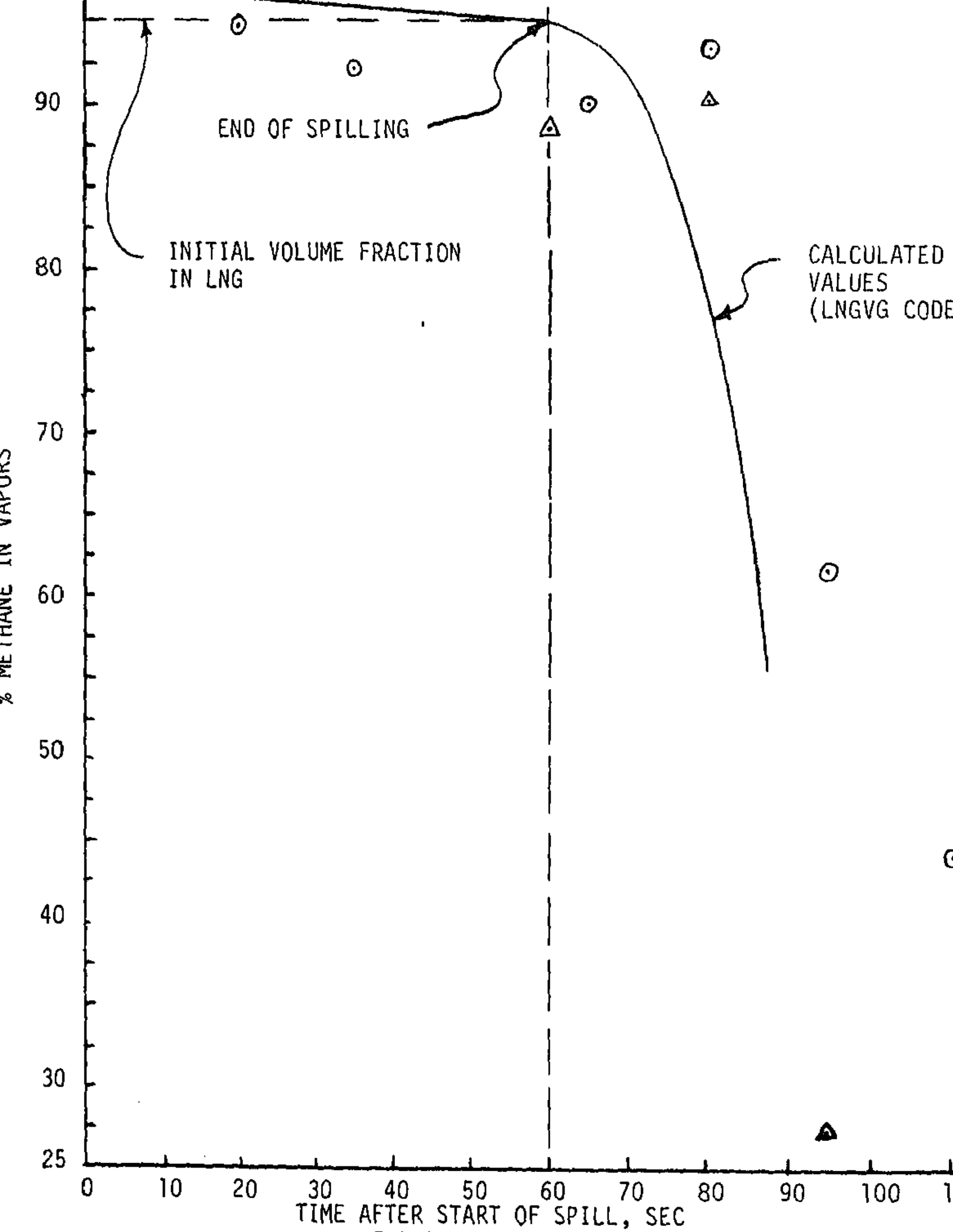
- STATION #2 DATA
CALCULATED
END OF SPILLING
NITIAL VOLUME FRACTION
N LNG
20
30
40
50
60
70
80
90
100
110
TIME AFTER SPILL START, SEC

FIGURE 3

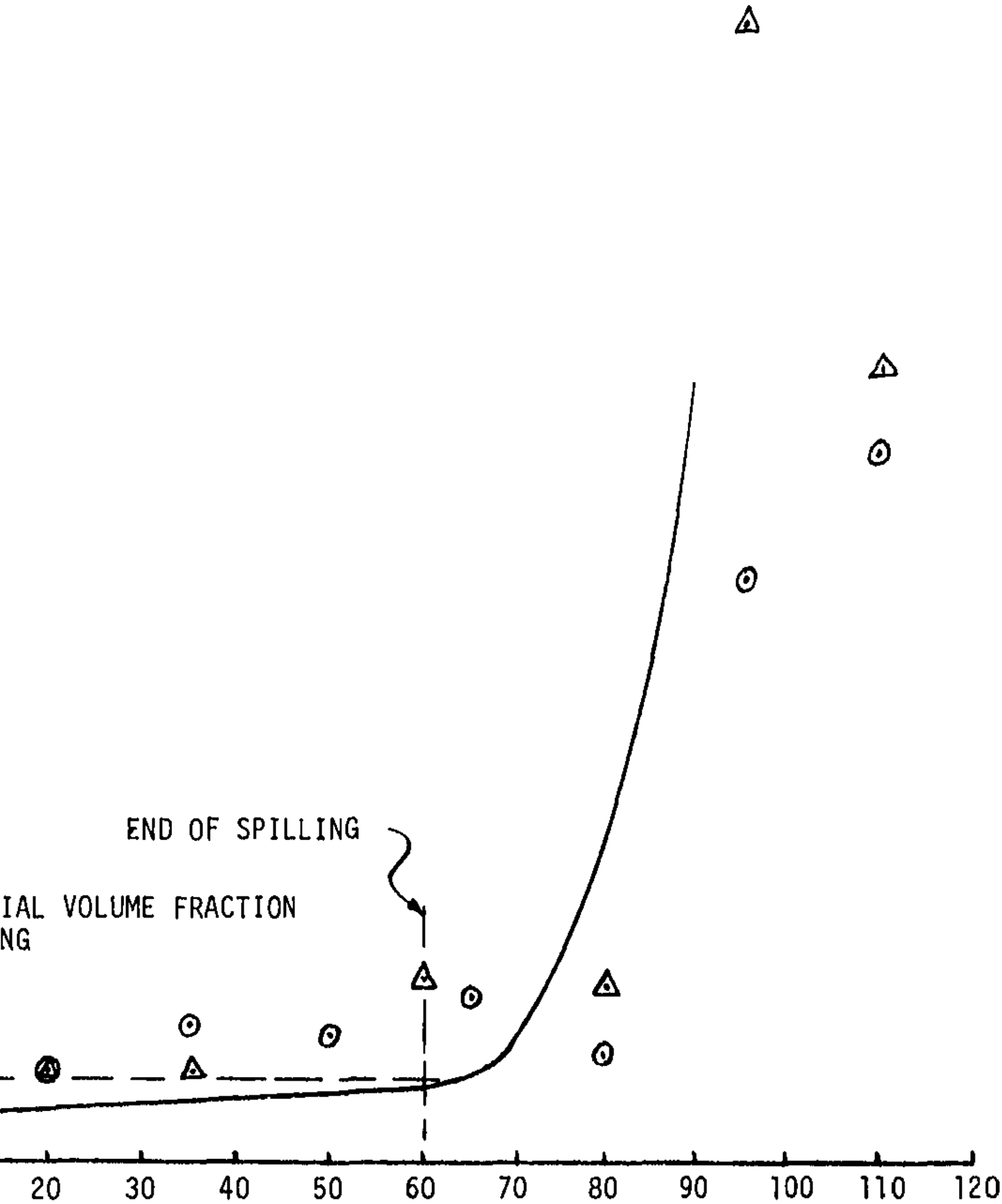


CALCULATED
END OF SPILLING
INITIAL VOLUME FRACTION
IN LNG
10
20
30
40
50
60
70
80
90
100
110
120
TIME AFTER SPILL START, SEC

F I G U R E   4

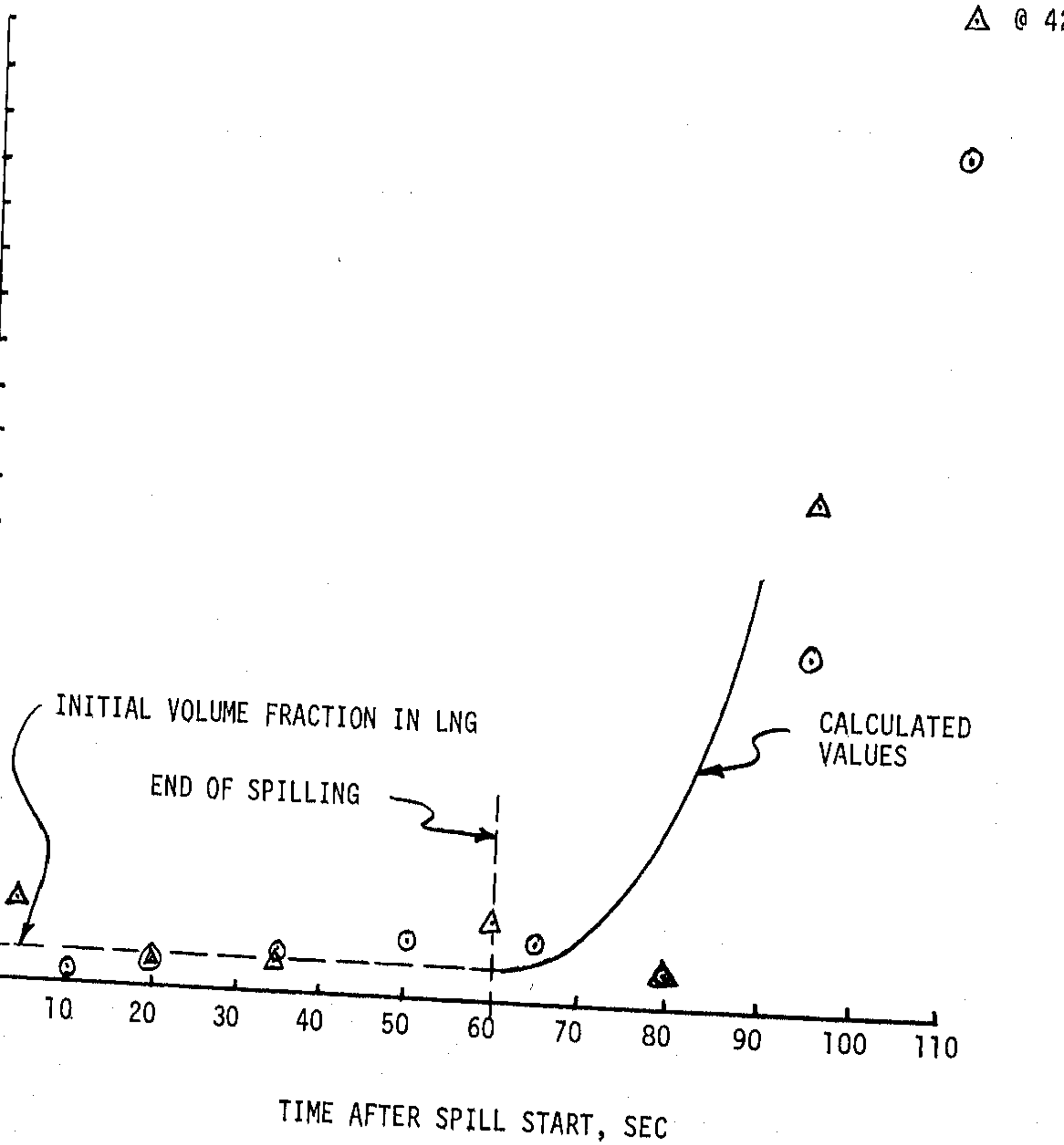

% METHANE IN VAPORS
90
80
70
60
50
40
30
25
INITIAL VOLUME FRACTION IN LNG
END OF SPILLING
CALCULATED VALUES (LNGVG CODE
0
10
20
30
40
50
60
70
80
90
100
TIME AFTER START OF SPILL, SEC

F I G U R E 5



END OF SPILLING
IAL VOLUME FRACTION
NG
20
30
40
50
60
70
80
90
100
110
120

FIGURE 6



△ @ 42
INITIAL VOLUME FRACTION IN LNG
END OF SPILLING
CALCULATED
VALUES
10
20
30
40
50
60
70
80
90
100
110
TIME AFTER SPILL START, SEC

FIGURE 7

INSTANTANEOUS LNG SPILL VOLUME-LIQUID

	10 M^3		1000 M^3	
ANALYSIS	RMAX(M)	TMAX(SEC)	RMAX(M)	TMAX(SEC)
LNGVG	20	44	113	111
FAY[5]	16	24	109	108
RAJ[4]	20	38	115	120

. Boyle, G. J., and Kneebone, A., "Laboratory Investigations into the Characteristics of LNG Spills on Water: Evaporation, Spreadin and Vapor Dispersion", Shell Research, Ltd., Report to A.P.I. Proj on LNG Spills on Water, Ref. 6Z32, March 1973.

3. W. G. May and P. V. K. Perumal, "The Spreading and Evaporation of LNG on Water", ASME Annual Winter Meeting, Nov. 17-22, 1974, N.Y., N.Y.

4. G. E. Feldhauer, et al., "Spills of LNG on Water-Vaporization and Downwind Drift of Combustible Mixtures", Esso Research and Eng., Co., Report No. EEGIE-72, Pg. 52; 24 May 1972.

5. P. K. Raj and A. S. Kalelkar, "Fire Hazard Presented by a Spreading, Burning Pool of Liquified Natural Gas on Water", Paper No. 73-25, Page 8, Western States Section/The Combustion Institute 1973 Fall Meeting.

6. J. A. Fay, "Unusual Fire Hazard of LNG Tanker Spills", Combustion Science and Technology, 1973, Vol. 7, pp. 47-49.

```
LNGVG(LNGIN,TAPE2=LNGIN,LNGOUT,TAPE3=LNGOUT)
ICE(6HCREATE,6HLNGOUT,50000)
ON RATE OF CONSTITUENT 1 OF THE LNG, FT/SEC
 CALCULATING A
NT (0.675)
IFIC HEAT OF CONSTITUENT I, BTU/LBM/F
ITY DIFF. BETWEEN WATER AND LNG ON WATER , LBM/CU.FT.
OLUME OF CONSTITUENT I VAPORIZED DURING A TIME STEP, CU.FT
TION OF DENSITY*VOLUME OF EACH LNG CONSTITUENT
AGE DENSITY OF LNG ON WATER
LUME OF CONSTITUENT I VAPORIZED PER SEC.,CU.FT./SEC
ME FRACTION OF CONSTITUENT I IN LNG VAPORIZED
UME FRACTION OF CONSTITUENT I IN LNG SUPPLIED
LUME FRACTION OF CONSTITUENT I IN REMAINING SPILLED LNG
ON OF GRAVITY - FT/SEC/SEC
HEIGHT OF LNG ON WATER SURFACE
NESS OF LNG AT START OF POOL BREAKUP, FT.
AT OF VAPORIZATION OF CONSTITUENT I, BTU/LBM
ANS CONTINUOUS SPILL. ICONT=0. FOR NON-CONTINUOUS SPILL
NS INSTANTANEOUS SPILL. INST=0. FOR NON-INSTANTANEOUS SPIL
 OF INPUT FILE
E OF OUTPUT FILE
IER OF PTIM TO OBTAIN PRINT-OUTS AT GREATER TIME INTERVALS
RGER THAN N1
ER OF PTIM TO OBTAIN PRINT-OUTS AT GREATER TIME INTERVALS
RGER THAN N2
IER OF PTIM TO OBTAIN PRINT-OUT AT GREATER TIME INTERVALS
TIONS ARE BEING MADE DURING POOL BREAK-UP
UMBER OF INCREMENTS FOR WHICH CALCULATIONS ARE MADE
UMBER OF TIME STEPS AT INCREMENTS OF STEP1,STEP2,STEP3 SEC
ER OF CONSTITUENTS COMPRISING THE LNG
NUMBER ASSOCIATED WITH ONE OF THE CONSTITUENTS OF LNG

N CALCULATIONS TO SET PRINT-OUT TIME INCREMENT
INTERVAL FOR PRINTOUT OF RESULTS, SEC
*A, FT/SEC
D OF QBFT(1) TO QBFT(I) TIMES 3.14
EAT TO VAPORIZE CONSTITUENT I ,BTU/LBM
F LNG POOL ON WATER SURFACE
IOR RADIUS OF POOL BREAK-UP
ITY OF POOL SPREAD, FT/SEC
SSION RATE OF LNG DURING VAPORIZATION, FT/SEC
SITY OF CONSTITUENT I, LBM/CU.FT.
TY OF WATER , LBM/CU.FT
ADIUS LNG POOL ATTAINS
 OF SPILL OF LNG, CU.FT/SEC
ENSITY OF LNG SUPPLIED, LB/CU.FT.
 DURATION OF SPILL, SEC
L TIME STEP USED IN CALCULATION, SEC
L VOLUME OF LNG VAPORIZED PER TIME STEP,CU.FT.
TAL VOLUME VAPORIZED OF CONSTITUENT I, CU.FT.
L VOLUME OF LNG VAPORIZED PER SEC., CU.FT./SEC
ROM START OF CALCULATION, SEC
AL TEMPERATURE OF LNG, DEGREES RANKINE
MPERATURE AT VAPORIZATION OF CONSTITUENT, DEGREES RANKINE
 VOLUME VAPORIZED, CU. FT.
F LNG ON WATER SURFACE, CU.FT.
 CALCULATIONS TO CALCULATE V
UME OF CONSTITUENT LEFT ON SPILL SURFACE, CU.FT.
AL VOLUME OF LNG SITTING ON WATER SURFACE TO START CALC'S
```

```
UNITS OF CU.FT.
 DIMENSION NUMBER(5),FRI(5),RHO(5),HVAP(5),TVAP(5),CP(5),QB(5),Q(5)
1,VOL(5),QBFT(5),DELV(5),FR(5),FRI(5),DLVS(5),TDLV(5)
 READ INPUT DATA
 READ(2,1000) INST,ICONT,NOSPE,N1,N2,N3,STEP1,STEP2,STEP3,G,RHOW,
1RSPIL,SPILT,VOLI,TNOT,REGR,HBRK,ROAV,CON,PTIM,M2,M3,M4
 WRITE OUT INPUT DATA
 WRITE(3,1020)
 WRITE(3,1030)
 WRITE(3,1040) INST,ICONT,NOSPE,N1,N2,N3,STEP1,STEP2,STEP3,G,RHOW,
1RSPIL,SPILT,VOLI,TNOT,REGR,HBRK,ROAV,PTIM,M2,M3,M4,CON
 WRITE(3,1050)
 DO 20 I=1,NOSPE
 READ(2,1010) NUMBER(I),FRI(I),RHO(I),HVAP(I),TVAP(I),CP(I)
 WRITE(3,1060) NUMBER(I),FRI(I),RHO(I),HVAP(I),TVAP(I),CP(I)
 CONTINUE
 AB=0.0
 INITIALIZE PARAMETERS
 DO 30 I=1,NOSPE
 QBFT(I)=(CP(I)*(TVAP(I)-TNOT)+HVAP(I))*RHO(I)
 VOL(I)=FRI(I)*VOLI
 AB=AB+(QBFT(1)/QBFT(I))*VOL(I)/VOLI
 QB(I)=QBFT(1)*3.14/QBFT(I)
 TDLV(I) = 0.000
 CONTINUE
 WRITE(3,1070)
R=(VOLI/3.14)**0.3333
DELRO=RHOW-ROAV
V=VOLI
H=R
A=REGR/AB
IF(ICONT.EQ.1) RMAX=(RSPIL/(3.14*REGR))**0.5
STEP=STEP1
N=N1+N2+N3
N2=N2+N1
VOL = 0.0000
T1 = 0.0000
IM = 0.0000
T=PTIM
DOT = 0
F(INST.EQ.1) RMAX=9999.
RITE(3,1080) TIM,N,RMAX,R,H,DELRO,A
O 40 I=1,NOSPE
(I)=QB(I)*A
RITE(3,1090) I,VOL(I),QBFT(I),QB(I)
ONTINUE
RITE(3,1100)
RANSIENT CONTINUOUS OR INSTANTANEOUS SPILL CALCULATIONS
 350 I=1,N
(I.GT.N1) STEP=STEP2
(I.GT.N2) STEP=STEP3
M=TIM+STEP
(TIM.GT.SPILT) RSPIL=0.0
(R.EQ.RMAX) GO TO 305
OT=CON*((G*DELRO /RHOW)**0.25)*(V**0.25) /(TIM**.5)
R+RDOT*STEP
(R.GE.RMAX) R=RMAX
(R.EQ.RMAX) RDOT = 0.000
(R.EQ.RMAX) IDOT = 1
ELV=0.0
```

```
J=1,NOSPE
=Q(J)*VOL(J)*(R**2)*STEP/V
VOL(J)+RSPIL*FRI(J)*STEP-DELV(J)
DELV+DELV(J)
OL(J)
NS+RHO(J)*VOL(J)
 = DELV(J)/STEP
E
 TDELV/STEP
TVOL + TDELV

ENS/V
HCW-DENS1
 4*(R**2))
M=1,NOSPE
=VOL(M)/V
ELV(M)/TDELV
 = TDLV(M) + DELV(M)
E
 N1) PTIM=PT*M2
 N2) PTIM=PT*M3
+STEP
 EQ.1) GO TO 347
 HBRK) GO TO 347
GE.PTIM) GO TO 347
49
E
 1110) I,TIM,R,H,DENS1,RDOT
 1115)
 1120) (J,VOL(J),DLVS(J),TDLV(J),FRI1(J),FR(J),J=1,NOSPE)
 1130) V,TDLVS,TVOL
 EQ.1) GO TO 348
 0000
0
E
 HBRK) GO TO 600
E

 1200)
 1210) RMAX,H,TIM
*M4

 =K,N
 N1) STEP=STEP2
 N2) STEP=STEP3
+STEP
MAX**2-(V/(HBRK*3.14)))**0.5
AX-RBRK)/RMAX
LT.0.01) GO TO 1660

 0
J=1,NOSPE
=Q(J)*(VOL(J)/V)*(RMAX**2-RBRK**2)*STEP
VOL(J)-DELV(J)
J).LT.0.0) VOL(J)=0.0
OL(J)
DELV+DELV(J)
 = DELV(J)/STEP
```

```
V.LE.0.0) GO TO 1660
620 M=1,NOSPE
M)=DELV(M)/TDELV
I(M)=VOL(M)/V
V(M) = TDLV(M) + DELV(M)
TINUE
=PT1+STEP
PT1.GE.PTIM) GO TO 630
TO 640
TINUE
TE(3,1220) I,TIM,RBRK
TE(3,1115)
TE(3,1120) (J,VOL(J),DLVS(J),TDLV(J),FRII(J),FR(J),J=1,NOSPE)
TE(3,1130) V,TDLVS,TVOL
=0.0
INUE
INUE
IAT(3I2,3I5,5F10.4,/,7F10.4,/,2F10.4,3I5)
IAT(I2,5F10.4)
IAT(1H1,"LNG VAPOR GENERATION FOR A SPILL ON WATER - W. STEIN")
IAT(//,2X,"INPUT PARAMETERS")
AT(/,5X,"INST=",I2,2X,"ICONT=",I2,2X,"NCSPE=",I2,2X,"N1=",I6,
N2=",I6,2X,"N3=",I6,/,5X,"STEP1=",F10.4,2X,"STEP2=",F10.4,2X,
P3=",F10.4,2X,"G=",F10.4,/,5X,"RHOW=",F10.4,2X,"RSPIL=",F10.4,
SPILT=",F10.4,/,5X,"VOLI=",F10.4,2X,"TNOT=",F10.4,2X,"REGR=",
4,/,5X,"HBRK=",F10.4,2X,"ROAV=",F10.4,2X,"PTIM=",F10.4,2X,
",I6,/,5X,"M3=",I6,2X,"M4=",I6,2X,"CON=",F10.4)
AT(//,6X,1HI,3X,6HFRI(I),4X,6HRHO(I),3X,7HHVAP(I),3X,
AP(I),5X,5HCP(I))
AT(5X,I2,5F10.4)
AT(//,2X,"INITIAL AND CALCULATED PARAMETERS AT TIME ZERO")
AT(/,5X,"TIM=",F10.4,2X,"N=",I6,2X,"RMAX=",F10.6,2X,"R="
S,/,5X,"H=",F10.6,2X,"DELRO=",F10.4,2X,"A=",F10.6)
AT(5X,"I=",I2,2X,"VOL(I)=",E12.6,2X,"QBFT(I)=",E12.6,2X,
)=",E12.4)
AT(1H1,2X,"TRANSIENT CALCULATIONAL OUTPUT")
AT(/,6X,"I",4X,"TIME",8X,"R",9X,"H",6X,"DENSITY",4X,"RDOT",/,
10.6)
T(15X,"VOL(I)",9X,"DLVS(I)",8X,"TDLV(I)",3X,"FRII(I)",4X,
I)")
T(2X,I6,3E15.6,2F10.6)
T(/,1X,"TOTALS",1X,3E15.6)
T(1H1,2X,"POOL BREAKUP CALCULATIONAL OUTPUT")
T(/,2X,"RMAX=",F10.6,2X,"HBRK=",F10.4,2X,"TIM=",F10.6)
T(/,2X,"I=",I6,2X,"TIME=",F10.4,2X,"RBRK=",F10.6)
(3,2000)
T(5X,"LNG HAS EVAPORATED - PROBLEM FINISHED")
T(5X,"MAX RADIUS ATTAINED AT TIME =",F10.6)
EXIT
```

B. R. Bowman

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract W-7405-Eng-48

Lawrence Livermore Laboratory
Livermore, California 94550

FIGURES

TABLE OF CONTENTS

FIGURES

SUMMARY

Proper modeling of the dispersion process following an LNG spi is critical to hazards evaluation and to the selection of terminal sites and shipping lanes. Predictions of the vapor generation and dispersion determine the downwind, lateral and vertical extent of flammable portions of the hydrocarbon/air mixture and provide initi conditions for deflagration or detonation calculations. These are to estimate the damage potential of a flammable cloud which might r from a liquid spill.

This report contains a status report on the modeling effort at Lawrence Livermore Laboratory and some comparisons of different mod used to predict dispersion. Two types of models are considered her The first is a version of one originally proposed by Germeles and D and the second type is in the form of two finite difference codes, and TDC, which solve the time dependent, compressible, conservation equations with turbulence. Results of these models are compared in terms of the predicted maximum distance to the lower flammability l as a function of liquid spill volume. Characteristic vertical prof of the models are also compared for a particular spill size. The m deficiency in all models to date is the unavailability of experimen data at several spill volumes with which to compare predictions.

A brief summary of current developmental work and that propose for the near future is also included.

INTRODUCTION

A number of dispersion models have been published which predict the downwind travel distance to the Lower Flammability Limit of a dispersing LNG vapor cloud.[1-7] These models vary in complexity as well as in basic assumptions used in their development, and with the exception of the SAI model,[7] have not been compared to data on LNG spills. Data used to verify the SAI model were taken by Battelle Columbus Laboratorie and the model/data comparison is given in reference 7. These data were collected for a 53 m^3 liquid spill within a dike. Unfortunately, the SAI report does not include contour plots of the vapor concentration so a good spatial comparison of the three dimensional SIGMET calculation ca be made with the data.

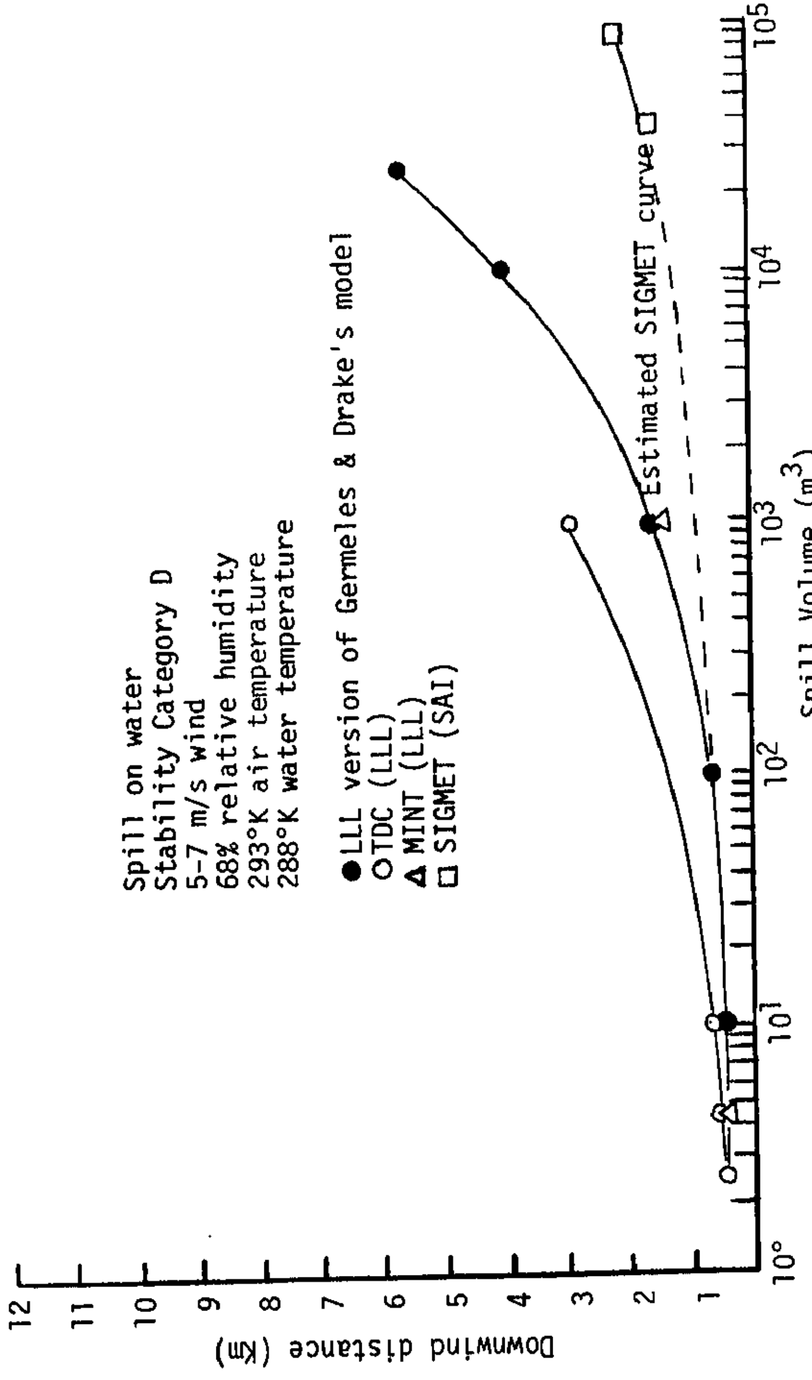
Havens[8] has published the results of a systematic evaluation of th models when they were exercised using similar, but not identical, input conditions. These models range in complexity from the classical gaussi solution to the incompressible form of the conservation of mass equatio (see reference 10 for example) to the time dependent solution of the turbulent three dimensional Navier-Stokes equations.[7] Havens concludes his study that the relatively simple model published by Germeles and Dr and the most complex model published by England et al.[10] represent the most rational approaches, of the models considered, to estimate the downwind dispersion of the vapor cloud.

Based on this recommendation, the approach taken here is to compar the results of models as a function of spill volume size.

The Germeles and Drake model described in reference 3, incorporates the vaporization model for a single constituent boil-off on water. This is used as an initial condition for the next phase of the model which accounts for the spread of the vapor under the influence of gravity. During the gravity spread phase, the flow is assumed to be expanding radially in one-dimension and models are included which calculate heat transfer from the ground, heat transfer from the air, the rate of a entrainment and condensation and freezing of the water vapor in the air. The wind shear has no influence on the problem in this phase so that the resulting distribution of LNG vapor and entrained air is a homogeneous cylinder. When the radial velocity reaches the wind velocity, it is assumed that gravity forces no longer dominate the problem and that furt dispersion may be treated in the classical gaussian fashion. Unfortunat the Germeles and Drake model assumes that the entire spill volume is dum instantaneously or that a continuous steady emission of vapor occurs fro the spill point. Neither of these cases is likely to occur in a typical situation. Therefore, a model that estimates dispersion from a source o finite time period is required to more closely approximate real situatio Two such models exist at LLL; however, these require large, fast compute obtain solutions. Both of the computer codes (MINT[11] and TDC[12]) numeric solve the complete three-dimensional equations of motion and include fir and second order models for turbulence. Solutions are for the compressi form of the equations in contrast to the incompressible solution reporte by England, et al.[10] For the dispersion calculations the incompressible code appears to be adequate and may be preferred because of lower comput costs. However, the use of a compressible code may be justified because

avoid problems of interfacing two separate codes when compu
combustion processes becomes necessary.

Havens has indicated that differences between the simp
Germeles and Drake) and the more complex models (MINT, TDC,
occur at relatively large spill volumes. If this is true,
might be formed for defining a minimum spill volume at whic
experiments should be conducted. A comparison of the maxim
the lower flammability limit as a function of spill volume
Fig. 1. Four plots are shown for calculations made using si
These plots compare the results from the LLL version of the
Drake model for the instantaneous spill case. Also shown ar
MINT and TDC both run in the two dimensional mode. The mode
agree fairly closely up to spill volumes of about 100 m^3 whe
giving longer LFL distances than the Germeles and Drake model
only large spill results were available for a SIGMET calculat
it is significant to note that the departure from the simple
very apparent. The more conservative values given by TDC are
two dimensional effect of the calculation which artificially
elongation of the cloud. Three dimensional calculations are
being made with both MINT and TDC which will be published in a
report. A preliminary result of one such calculation is shown
which compares the configuration of the 5% contour for MINT, r
2-D and 3-D mode, and for the two options available in the Ger
Drake code for a continuous and an instantaneous spill. These
are plotted on the centerline for a 5 m^3 liquid spill dispersi
wind. The code calculations are made for a spill rate of 5 m^3


Spill on water
Stability Category D
5-7 m/s wind
68% relative humidity
293°K air temperature
288°K water temperature
LLL version of Germeles & Drake's model
TDC (LLL)
MINT (LLL)
SIGMET (SAI)
Estimated SIGMET curve
Downwind distance (Km)
12
11
10
9
8
7
6
5
4
3
2
1
10°
10¹
10²
10³
10⁴
10⁵

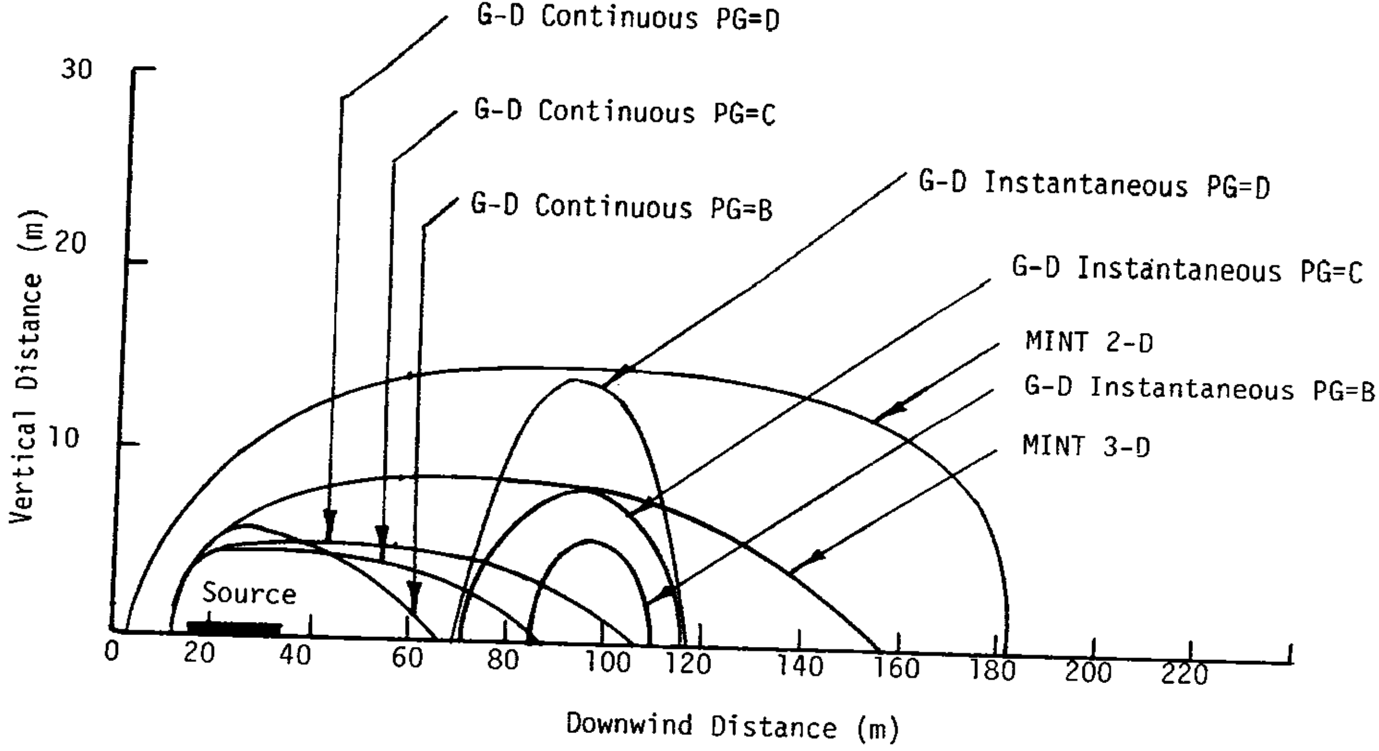


Fig. 2 5% Isopleths at 40 sec with 7 m/s wind comparing MINT, and Germeles and Drake's model (G-D refers to Germeles and Drake plot; PG = refers to Pasquill Gifford Stability Category)

1. Burgess, D. S., J. N. Murphy, and M. G. Zabetakis, "Hazards o
Spillage in Marine Transportation," U.S. Bureau of Mines, per
for the U.S. Coast Guard (NTIS AD-705078) 1970.

2. Burgess, D. S., J. Biordi, and J. Murphy, "Hazards of Spillag
LNG into Water," U.S. Bureau of Mines, performed for the U.S.
Guard (NTIS AD-754498) 1972.

3. Germeles, A. E. and E. M. Drake, "Gravity Spreading and Atmos
Dispersion of LNG Vapor Clouds," Fourth International Symposi
Transport of Hazardous Cargoes by Sea and Inland Waterways, s
by U.S. Department of Transportation (U.S. Coast Guard), Jack
Florida 26-30 October 1975.

4. Raj, P. P. K. and A. S. Kalelkar, "Assessment Models in Suppo
of the Hazards Assessment Handbook (CG-446-3)," prepared for
U.S. Coast Guard January 1974 (NTIS AD 776617).

5. Fay, James A. and David H. Lewis, Jr., "The Inflammability an
Dispersion of LNG Vapor Clouds," Fourth International Symposi
on Transport of Hazardous Cargoes by Sea and Inland Waterways
sponsored by U.S. Coast Guard, Jacksonville, Florida 26-30 Oc
1975.

6. "DRAFT Environmental Impact Statement for the Construction an
Operation of an LNG Receiving Terminal at Los Angeles, Califo
Volume II," Federal Power Commission, Western LNG Terminal As
Docket No. CP 75-83-2 (September 1976).

7. "LNG Terminal Risk Assessment Study for Oxnard, California,"
Applications, Incorporated, 1200 Prospect Street, La Jolla, C
92037, prepared for Western LNG Terminal Company, 720 West Ei
Street, Los Angeles, California 90017 (December 22, 1975).

8. J. A. Havens,"Predictability of LNG Vapor Dispersion from Cat
Spills onto Water: An Assessment," DOT document CG-M-09-77, A

9. G. T. Csanady, Turbulent Diffusion in the Environment, D. Rie

10. W. G. England, L. H. Teuscher, L. E. Hauser, and B. E. Freema
spheric Dispersion of Liquefied Natural Gas Vapor Clouds usin
a Three-Dimensional Time-Dependent Hydrodynamic Computer Code
of the 1978 Heat Transfer and Fluid Mechanics Institute, June

11. H. J. Gibeling, H. McDonald, and W. R. Briley, "Development o
Dimensional Combustor Flow Analysis," Vol. I, II, and III, AF
Technical Report TR-75-59 (1974 - 1976).

12. L. C. Haselman, "TDC - A Computer Code for Calculating Gaseou
bustion in Two Dimensions," Lawrence Livermore Laboratory rep
to be published.

REPORT C

Test Cases for a Phase I Evaluation of LNG Vapor Generation and Dispersion Models

D. J. McNaughton
C. M. Berkowitz

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352
Operated by Battelle Memorial Institute

The report provides a systematic means for a comparative evaluation of
main features of LNG vapor generation and dispersion models using detai
riptions of the models and the results produced by the models when exce
elected test cases. A form for recording model description information
eveloped to ensure uniformity of detail and a standard format for the
rmation. Analytical test cases were selected based on experimental des
ods in an attempt to minimize the number of test cases required to study
parameter effects and parameter interactions. A second set of model
cases could be generated to refine the evaluation of the formulations o
meters modeled.

A number of LNG vapor generation and dispersion models currently exi
st reviews of LNG vapor generation and dispersion models (e.g., Havens,
77) have shown wide divergence of model solutions when applied to simil
ts of input conditions.

Current experimental information is apparently inadequate to resolve
ese differences. An analytical comparative evaluation of the models wo
useful for two reasons: 1) it could likely identify the cause of some
e divergence and permit some solutions to be discounted for improper tr
the physical processes involved, and 2) it could provide information o
portance and sensitivity of parameters to guide future experimental eff
validation of the models. In order to perform this evaluation, base e
d assumptions should be specified in a consistent, easily comparable fo
d results should be calculated to demonstrate main parameter effects an
teractions in the various formulations. This report details the first
a two phase approach to provide input to perform such an evaluation.

The two phase approach allows early use of some evaluation results w
suring that the evaluation accounts for all important aspects of the va
neration and dispersion problem as described by the different models.
ase I, model descriptions and initial test case results are compared.
jective of initial test case simulations is evaluation through comparis
model results. Analyses of test case results would clarify further mo
velopment studies and aid in experimental planning by indicating critic
eas of scale and variable interactions. Phase I results would also be
ailable to design Phase II test cases which would provide more refined
nsitivity tests and some validation studies for limited parameter range
lected parameters. Together the two phases would completely describe t
dels and identify sensitive parameters requiring further analytical and
perimental study.

Section 2 of this report provides a description of the data formats
ggested for the model descriptions. Section 3 contains a discussion of
st case development and the case variables, along with a consistent set

of constants specific to each of four components areas of LNG vapor
tion and dispersion: pool spreading, vapor generation, cloud sprea
cloud dispersion. A fourth section describes some important conside
in use of this report.

An important part of model evaluation and comparison is a complet description of model components, parameters and numerical methods. Th section contains a table which could be used to supplement model descr reports to summarize in a consistent manner LNG vapor generation and d simulation models.

Table 1 presents a model description questionnaire which could be to facilitate the comparison of complete LNG vapor generation and disp models or models of separate components of the problem. Multi-use mod (i.e., land spill versus water spill) can be evaluated by filling out form for each type of model application.

The table has been structured in three parts: 1) a description o parameters, 2) a list of processes, and 3) space for descriptions of b equations categorized by the four components of LNG vapor generation a dispersion models. The first two parts of the table list in a column, meters and processes included in LNG vapor generation and dispersion, rows, four components of LNG vapor generation and dispersion; pool spr evaporation, gravity spread of a vapor cloud, and vapor dispersion. T table includes space for variables and processes not included in the c listing.

Table entries are made using the descriptor codes found in Table For each table entry, one of the descriptors from both the parameter c group and the time dependence code group should be used. The codes in which parameterizations are in the models, how various parameters are in conjunction with the time dependence codes, whether parameters and are fixed in time or vary with time. For example, the spill codes dis models with continuous spills rather than instantaneous spills, or sho use of time dependent gravity spread models with steady-state Gaussian dispersion models.

The final section of Table 1 requires a description of base equ
used in simulating each phase of vapor generation and dispersion and
numerical approaches have been followed. Equations or comments shou
individually numbered in sequence so they can be referred to by descr
in the first two sections of the table.

Parameters	Evaporation	Pool Spread	Cloud Spread	Dispersion
	Model Components			
0 Spill Characteristics				
1.1 Magnitude				
1.2 Shape/Area - LNG Pool				
1.4 Depth				
1.5 Confinement[a]				
1.6				
0 Substrate Characteristics Land Spills				
2.1 Moisture Content				
2.2 Heat Transfer Coeff.				
2.3 Substrate Density				
2.4 Substrate Slope				
2.5 Substrate Heat Capacity				
2.6 Substrate Thermal Diffusivity				
2.7 Substrate Temperature				
2.8				
Water Spills				
2.11 Water Temperature				
2.12 Water Depth				
2.13 Density Variations in Water				
2.14 Thermal Characteristics of Water				
2.15 Convective Heat Transfer Through Water				
2.16 Heat of Fusion				
2.17				

Parameters	Evaporation	Pool Spread	Cloud Spread	Dis
	Model Components			
3.0 <u>LNG Characteristics</u>				
3.1 Composition Density Specific Heat				
3.2 Temperature				
3.3 Boiling Temperature				
3.4				
4.0 <u>Atmospheric Characteristics</u>				
4.1 Wind Speed				
4.2 Ambient Temperature				
4.3 Solar Radiation				
4.4 Surface Roughness				
4.5 Stability				
Eddy Diffusivities				
Dispersion Parameters				
4.6 Humidity				
4.7				
5.0 <u>Vapor Cloud Characteristics</u>				
5.1 Shape/Area - LNG Vapor Cloud				
5.2 Distance to LFL				
5.3 Concentration				
5.4 Density				
5.5				

Parameters	Model Components: Evaporation	Pool Spread	Cloud Spread	Dispers
6.0 Processes				
6.1 Pool Breakup				
Dike Filling				
6.2 Ice Formation				
6.3 Ice Layer Growth				
6.4 Water Turbulence				
6.5 LNG Encapsulation				
6.6 Film Boiling				
6.7 Nucleate Boiling				
6.8 Freezing of Soil				
6.9 Soil Cracking				
6.10 Modification of Ambient Air Boundary by Vapor Cloud				
6.11 Modification of Dispersion Parameters by Vapor Clouds				
6.12 Radiational Heat Addition to Pool (Solar)				
6.13 Radiational Heat Addition to Cloud (Solar)				
6.14 Water Pickup (Atomization)				
6.15 Surface Heating of Vapor Cloud				
6.16 Entrainment of the Vapor Cloud				
Sensible Heat Transfer				
Latent Heat Transfer				
6.17				

Base Equations

7.0 LNG Pool Spread

8.0 LNG Evaporization

9.0 LNG Cloud Spread

10.0 LNG Dispersion

11.0 Comments:

Cn.n - Parameter calculated in process or numerical expression n.n[a][b]

S - Parameter specified

Blank - Parameter not in model

O - Output result

Pn.n - Parameter implicit in parameter or process n.n

Time Dependence Codes

CS - Constant Effect, Process or Use (Point values e.g., spill volume)

SS - Steady-State or Continuous Effect Process or Use (Rates, rate equations e.g., spill rate)

TV - Time Varying Effect Process or Use

(a) n.n refers to the table entries in Table 1. (e.g., 1.1 refers to spill magnitude.

(b) For example spill magnitude may be specified S, for the evaporation and pool spread submodels but may be calculated C7.0, C8.0 using pool spread and evaporation model for the cloud spread submodel. That is:

	Evaporation	Pool Spread	Cloud Sp
1.1 Spill Magnitude	S	S	C7.(

AND SENSITIVITY STUDIES

Understanding of a complex physical problem such as LNG vapor genera
d dispersion usually requires simplification to dominant parameter effe
rough the use of simulation models. Often selection of dominant parame
difficult due to the interactions of independent parameters, and vario
del development groups will interpret these interactions with different
rmulations. The main purpose of model evaluation is to demonstrate the
fferences or similarities among models and to demonstrate the capabilit
the formulations in describing the real physical progress intended. M
nsitivity, a component of model evaluation, provides a means of measuri
rameter effects and interactions in models at each point in the respons
nction and can aid in establishing applicability. Analyses of model res
lculated from initial test cases presented in this section could be use
del evaluation and in limited model sensitivity studies.

The LNG vapor generation and dispersion problem has been divided int
ur component sections:

- LNG Pool Spreading
- LNG Vapor Generation
- Gravity Spreading of LNG Vapor Clouds
- LNG Vapor Cloud Dispersion

ese components are mutually dependent and may prove inseparable in some
isting models, but this component analysis can aid in providing meaning
mparisons among most models. Model results generated for each componen
each model considered are comparable.

The cases specified may include components or parameters involved in
G vapor generation and dispersion that are not included in the models.
ese cases, tests can be made with reduced numbers of variables.

Selection of model test cases was made using methods similar to thos
ployed in experimental design rather than selecting a sequence of value
r each parameter of interest. Good experimental design methods object

experiments provides cost and time savings and reduces the volume of co... data while assuring that the tests produce sufficient results for analys... Applying experimental design methods to model evaluation testing is stra... forward and involves only the deletion of replicate cases which would no... be included in experiments to determine experimental error and reproduci...

For this study, test cases were selected on the basis of response s... experimental designs (DuPont, 1975). The methods measure the response o... or more dependent variables to changes in a number of independent variab... The methods adopted for this application are the three and four paramete... Box-Behnken designs; these methods provide information on parameter inte... extreme value responses or dominant parameter effects, and curvature of ... response lines and variable surfaces over the range of expected paramete... magnitudes for continuous or piecewise continuous response functions. B... technique, regions of strong interactions are located using response sur... mapping providing preliminary sensitivity information.

In a complete sensitivity study, the measure of sensitivity is give... by:

$$\left.\frac{\partial x}{\partial a}\right|_{a_i},$$

i.e., the local change of dependent variable x responding to a change in... independent variable a at each value of a, ai. The derivative may vary ... the expected range of the variable, a, so that testing must be undertake... all a_i or at least over the region of model applicability. The prelimin... analyses of the test cases suggested can provide information on

$$\frac{\Delta x}{\Delta a}$$

evaluated between extremes of the parameter range and the midpoint in th... parameter range. It can therefore identify broad regions of model sensit...

ad to an identification of a polynomial response model for prediction assessment, via an analysis of variance, of the predictability of the erived model. In a model comparison study without validation, no real formation is available as a base for model comparison and development atistical model, but analysis of the data derived from the experimenta esign applied to exercising models can be quite useful. The analysis valuation will consist of a qualitative comparison of response surfaces teractions by examining the surface mapping of the responses, followed analysis and comparison of the variance in predictions among models. atistical analysis of variance will allow determination as to whether odel responses from the test cases presented in this section result fro arameter changes or from additional model parameters which should be co a second phase of testing. Comparison of variance in predictions amo odels will determine objectively which models are predicting the same iven identical test cases and which differ in response due to other pa eters which mask the effects caused by the test case parameters. This nalysis would highlight similarities and differences in models providi ategorization based on performance. The predictive capability of the elative to their complexity can be studied to determine the return resu rom additional sophistication. Identification of similar and differen ill simplify final model verification when data become available to de he predictive capability of the models.

The steps used in initial test case development for model evaluati re:

- Identification of parameters involved in each component of LNG vapor generation and dispersion
- Determination of the qualitative importance of the parameters based on previous results and literature.
- Determination of a range of parameter values. In the development of parameter ranges, it is important that the characteristics of current or proposed facilities be included.

In the last step, the number of variables is limited so that 3 and 4 va
Box-Behnken designs could be used. Normally for experiments these desi
would require 15 and 27 tests. Since the tests to determine experiment
error are deleted, 13 and 25 tests for each component are required. Th
following sections describe the test case definitions for each model co

3.1 LNG POOL SPREADING

Analytical studies of LNG pool spreading have centered on the case
water spills (it is assumed that during land spills, LNG would be conta
in a fixed impoundment area). Limited spread experiments on land have
performed (Japan Gas Association, 1974) but results were not quantified
a spread model. Some parameters of importance to the land spill spreadi
problem are terrain slope, surface roughness, loss of LNG in the soil,
to flow and total evaporation time. For this initial study, the spread
after a landspill is not considered.

Parameters for liquid spreading in a water spill are given in Tabl
The dependent variables in the water spill problem are normally pool re
rate, maximum LNG pool radius, and maximum time to final pool spread.
pool spread models for water spills are typically formulated as a densi
intrusion where outward radial motion is a result of hydrostatic force
adjust the density difference between the LNG and the water surface.

3.1.1 Test Cases

Parameters in the pool spread problem are reduced to three from th
presented in Table 3 based on known model capabilities obtained from op
references. These variables are spill volume, evaporational losses, an
composition or density differences. Test cases are assumed to be uncon
(in keeping with the generalized model formulations available for water
and instantaneous (since the single model found in surveying the litera
had a time dependent pool spread equation [Havens, 1977], which could b
used both for instantaneous or continuous spills with only slight modif

Spill Volume	
LNG Density/Composition	
Evaporational Losses	
Surface Roughness:	Water Viscosity Ice Layers Waves
Degree of Confinement	
Spill Configuration:	Instantaneous Continuous
LNG Pool Depth	

In general, surface roughness of the LNG/water interface is small anc and final LNG pool thickness are assumed to be constant in the test i to bound calculations of maximum pool spread and spread time.

The ranges of the three selected variables follow:

Spill Volume:	50 m^3 to 25,000 m^3
LNG Density:	4.5 kg m^{-3} to 470 kg m^{-3}
Evaporational Losses:	0.05 kg $s^{-1}m^{-2}$ to 0.20 kg $s^{-1}m^{-}$

Spill volumes range from the largest historical spill experiments (AG to a common size for single large shipboard LNG tank. LNG density ra reflect spills of 100% liquid methane to a mix of 65% liquid methane liquid ethane. The latter mix would demonstrate the effects of aged containing heavier gas components. Evaporational losses range from with ice formation included in the heat transfer to those where no ic formed (Opschoor, 1977).

Substitution of the variables in a three parameter experimental provides the test cases Table 4. The cases make use of parameter ra extremes and midpoints. The spill volume midpoint is a geometrical its value is in the region of maximum experimental spills discussed 1976 Workshop on LNG Safety and Control (DOE, 1978). For this analy constants specified in Table 5 will be used where required.

1	25,000	470	0.13
2	25,000	415	0.13
3	50	470	0.13
4	50	415	0.13
5	25,000	443	0.20
6	25,000	443	0.05
7	50	443	0.20
8	50	443	0.05
9	1,100	470	0.20
10	1,100	470	0.05
11	1,100	415	0.20
12	1,100	415	0.05
13	1,100	470	0.13

TABLE 5. Possible Pool Spread Constants

Final Pool Thickness	1.5×10^{-4} m (Boyle and Kneebone, 1973)
Gravitational Acceleration	9.8 m s^{-2}
Density of Water	1.0 kg l^{-1}
Density of LNG[(a)]	0.415 kg l^{-1}
Evaporation Rate[(a)]	0.13 kg s^{-1} m^{-2}

(a) Used when the parameter is not variable in the model.

Results for comparisons calculated from these cases would include m spill radius and the time required for a pool to spread to minimum thick

3.2 LNG VAPOR GENERATION

As an LNG spill spreads over a land or water surface, vapors are co ously emitted until the liquid is completely evaporated. The rate of ev tion (defined here as vapor generation per unit area) is a function of t

ation rate for water spills will depend primarily on convective heat er through the water and from possible ice formation. On land, high l rates result from initial contact of the LNG with the spill surface, s cooling of the substrate occurs, heat transfer and therefore evaporat ses with time. This large temporal variation is not as obvious in wate due to the turbulent mixing of the water.

he discussion of total vapor generation from a spill is incomplete with ltaneous description of evaporation rate, pool spreading, and confineme porated LNG vapors by dikes or terrain, since calculation of downwind ncentrations requires knowledge of the total source strength. For the e of initial model comparison and testing, test cases with evaporation s the dependent variable were selected to show the most important and ble effect in vapor generation. The effect of evaporation on pool ing is provided in the previous section. Table 6 presents a list of les involved with the calculation of LNG evaporation.

Test Cases

NG evaporation is largely dependent on two separate mechanisms for land ter spills (conduction vs. convection) therefore, two separate sets t cases are presented. The test case set for water examines the effect pool depth (a measure of spill quantity), water temperature, and water LNG land spill cases examine the effects of LNG depth, substrate ature, substrate conductivity and soil moisture. Both land and water consider confined spills to show the possible heating effects caused formation.

everal parameters presented in Table 6 were not considered for the l test sets. Most evaporation models are time dependent so only slight cations would be required to show the effects of continuous versus taneous spills. Variation of LNG composition and state of boiling may licit in the existing codes or can be considered in second generation ases. Substrate cracking, heat addition from the air and radiation, mospheric pressure variations appear to be secondary effects.

TABLE 6. Parameters Involved in Vapor Generation

Spill Characteristics:	Quantity Land/Water Confined/Unconfined Continuous/Instantaneous LNG Composition
Water Substrate:	Depth Temperature Ice Formation Ice Thickness
Land Substrate:	Temperature Water Content Conductivity Cracking
Heat Addition by Radiation.	
Heat Addition by Air.	
Atmospheric Pressure.	
Stage of Boiling:	Film/Nucleate

The initial test cases for water are presented in Table 7(a) and tho for land spills in Table 7(b). Test cases represent 3 or 4 parameter Box Behnken designs using variable ranges and midpoints. LNG spill depths ra from 0.15 m, approximating experimental spill depths (AGA, 1973) to 30 m land or 10 m on water. The larger depths reflect typical storage tank he simulating evaporation following the collapse of a tank roof for the land spill or partial confinement of LNG on water. Substrate temperatures are the range of typical sea surface or soil temperatures. Conductivities ra from 0.1 W m^{-1} s^{-1} typical of dry polyurethane to a value of 6 W m^{-1} s^{-1} for soil (Reid, 1978). Soil is assumed to have a moisture content range 0 to 25%. Midpoints for water depth, substrate conductivity, and LNG dep on land are based on a logarithmic scale.

Specified and assumed constants for the evaporation tests are given Table 8. Results should show evaporation rate by a function of time unti the liquid is totally evaporated.

Pool Depth (Water)[a]	5.0 m
Water Temperature[a]	290°k
Land Temperature[a]	296°k
Substrate Conductivity[a]	0.77 W m^{-1} K^{-1}
Soil Moisture[a]	13% (Dry Basis)
Water of Depth[a]	32 m
Conductivity from Air	0
Radiational Heating of Pool	0
LNG Composition	100% Methane

(a) Used when not variable in model

3.3 GRAVITY SPREADING OF LNG VAPOR CLOUDS

During the evaporation of spilled LNG, vapors form a dense cold vapo cloud which spreads radially from the spill site as a result of the densi difference between the cloud and ambient air. Spreading dominated by gra is thought to continue until the cloud density becomes equal to the densi of the ambient air. Dilution of the cloud to reach air density can resul through either heating of the cloud by entrainment of warm air, solar rad ation, heating by the condensation of atmospheric moisture (humidity) or heating from the ground. The main parameters in cloud spreading are give Table 9.

3.3.1 Test Cases

Model calculations for gravity spread of LNG vapor clouds normally a for the described tests provide extimates of the maximum gravity spread r which is defined as the radius at which the cloud density becomes equal t the ambient air density. This radius is the dependent variable in test c simulations developed in this study. The independent parameters selected to calculate the radius are cloud volume, initial cloud gas density, and input to the cloud. Test cases derived for these variables are listed in Table 10. All tests assume a flat frictionless surface, instantaneous

TABLE 9. Parameters Involved with LNG Vapor Cloud Spreading

Density:	LNG Composition Water Pickup Cloud Temperature
Spill Size:	Volume/Rate Cloud Depth
Spill Configuration:	Land Spill/Water Spill Terrain Slope Continuous Spill/Instantaneous Spill Obstruction to Flow Surface Roughness
Dilution:	Entrainment Heat Addition to the Cloud

TABLE 10. Three Parameter Test Designs for LNG Vapor Cloud Spread

Test	Initial Cloud Volume (m^3)	Initial Cloud Density ($g\ m^{-3}$)	Heat Addition to the Cloud ($kcal\ m^{-2}s^{-1}$)
1	1.5×10^7	2000	3.5
2	1.5×10^7	1800	3.5
3	6.0×10^4	2000	3.5
4	6.0×10^4	1800	3.5
5	1.5×10^7	1900	7
6	1.5×10^7	1900	0
7	6.0×10^4	1900	7
8	6.0×10^4	1900	0
9	7.5×10^6	2000	7
10	7.5×10^6	2000	0
11	7.5×10^6	1800	7
12	7.5×10^6	1800	0
13	7.5×10^6	1900	3.5

due to water pick up or changes in LNG composition are implicitly inclu in the other variables and the magnitude of their effects would possibl be examined using Phase II test cases.

Variables ranges on LNG cloud depth reflect approximate heights fo spills of 100 m^3 and 25,000 m^3 and the initial cloud is assumed to be a cylinder with radius equal to the pool size. LNG density variations range from the density of a 100% methane cloud at -160°C to the density 100% ethane cloud at -88°C. LNG density ranges were selected to show t effects of differential evaporation of LNG components on gravity spread addition to the cloud was calculated to approximate dilution effects ca by cloud heating from moisture condensation, radiation, or surface hea or a combination of effects. Some estimates of this heat flux can be derived from the San Clemente Data (AGA, 1973). Specified constants ar in Table 11.

TABLE 11. Possible Constants for Gravity Spread Models

Relative Humidity	0
Radiational Heating of the Cloud	0
Air Temperature	290°k
Heat Addition to the Clouds[(a)] (from all effects)	3.5 kcal m^{-2} s^{-1}
Initial Cloud Density[(a)]	1800 g m^{-3}
Wind Speed	0
LNG Composition	100% Methane

(a) Used when parameter is not specified in the model

3.4 LNG VAPOR CLOUD DISPERSION

Following an LNG spill sequence of pool spread, vapor generation vapor cloud gravity spreading, atmospheric dispersion acts to further the vapor cloud to concentrations below the lower flammability of the

of wind speed, surface roughness and some measure of atmospheric stabi
The first two variables define the mixing due to mechanically induced
while atmospheric stability measures the mixing due to thermal or buoy
induced turbulence.

LNG vapor dispersion models generally are a by-product of air qua
modeling work where diffusion of neutrally buoyant tracers is conside
In LNG spills, the vapor cloud is negatively buoyant which greatly mod
dispersion in the ambient environment. Existing LNG models attempt to
for this effect by either the use of a gravity spread model (Section 3
by corrections in the model dispersion equations. Test cases develope
this section can be used in calculations where gas dispersion equatior
used after a gravity spread submodel and also where gravity spread is
as a correction within the dispersion equations.

Parameters and processes included in the LNG dispersion problem a
given in Table 12. The calculational objective of most LNG vapor gene
and dispersion models is the determination of the distances in which t
cloud is hazardous. In the model evaluation the dependent parameters
calculations will be the downwind distances at which methane concentra
become 2% and 5% (by volume) in air. These distances would affect max
exclusion distances. Crosswind extent would be studied with Phase II
cases.

TABLE 12. Variables in LNG Vapor Dispersion

Spill Area	
Spill Volume/Rate	
Source Configuration:	Land/Water Continuous/Instantaneous
Atmospheric Mixing:	Stability Other Measures
Heat Addition to the LNG Vapor Cloud	
Gravity Spread	
Wind Speed	

e to the parameters which cannot be considered continuous, such as land rsus water and continuous versus instantaneous spills. For the initial st cases, these discrete parameters have been specified at constant value simplify analysis. The cases presented are for land spills with specif ill rate or volume (continuous or instantaneous) but variable spill areas e parameters selected for testing are spill area, atmospheric stability, nd speed, and heat addition to the vapor cloud. Land spills were chosen cause dispersion over land and water differs only by the turbulent mixing sponse to lower surface roughness over water and vapor cloud heating by nd or water surface. The extremes in either case can be approximated wi nd spill parameters. Test cases for continuous and instantaneous spill dels are combined using a single parameter spill area and specified spil lumes or rates. Spill areas range from point sources to the spill area rresponding to a spill radius of 950 m determined by Germeles and Drake avens, 1977) for a 25,000 m^3 spill volume. Use of this radius gives a r spills that could include estimates of gravity spread, initial cloud si confinement. The specified spill volume is 25,000 m^3 and the specified ill rate is 250 m^3 s^{-1} (25,000 m^3 over approximately 100 seconds, the ti ven by Fay for total evaporation time of a water spill [Havens, 1977] an therefore a lower bound on evaporation time).

Estimates of wind speed used include low to moderate values (1-15 m s abilities are given as (extremely) stable, neutral, and unstable to show e effects of unstable land spills and very stable sea spills. Heat dition ranges from zero to that which includes probable heat input from lar radiation, entrainment of warm air, condensation of atmospheric isture, and surface heating (5 kcal m^{-2} s^{-1}).

Table 13 displays a four parameter Box-Behnken design for the selecte arameters. Midpoints where selected linearly in all cases except for win peed where emphasis is placed in low wind speed categories and the geomet al mean was used. Constants specified or assumed for these tests are giv n Table 14. Simulation results should include maximum distances to flamm ility limits at 2% and 5% (by volume) methane.

Components of LNG Models

Test	Spill Radius (m)	Wind Speed (m s^{-1})	Stability	Heat (kcal s Additio
1	950	15	Neutral	2.5
2	950	1	Neutral	2.5
3	0	15	Neutral	2.5
4	0	1	Neutral	2.5
5	475	4	Unstable	5
6	475	4	Unstable	0
7	475	4	Stable(a)	5
8	475	4	Stable	0
9	950	4	Neutral	5
10	950	4	Neutral	0
11	0	4	Neutral	5
12	0	4	Neutral	0
13	475	15	Unstable	2.5
14	475	15	Stable	2.5
15	475	1	Unstable	2.5
16	475	1	Stable	2.5
17	950	4	Unstable	2.5
18	950	4	Stable	2.5
19	0	4	Unstable	2.5
20	0	4	Stable	2.5
21	475	15	Neutral	5
22	475	15	Neutral	0
23	475	1	Neutral	5
24	475	1	Neutral	0
25	475	4	Neutral	2.5

(a) Extremely stable (Pasquill - Turner Class F)

TABLE 14. Possible Constants for Vapor Dispersion Simulations

Heat Addition to the Cloud[a]	2.5 kcal s^{-1}
Spill Radius[a]	475 m
Stability[a]	Neutral
LNG Composition	100% Methane
Ambient Temperature	290°K
Atmospheric Pressure	1013 mb

(a) Used when parameter is not specified in the r

The model evaluation table and initial test cases presented in previ ctions cannot be applied directly to all LNG vapor generation and dispe dels, but they are sufficiently general so that only slight modificatio codes would be required to provide simulation results. Several expect fficulties in applying the description tables and test cases are discus this section.

Application of the model evaluation table in Section 2.0 may be comp ted if either parameter or process listings exclude effects deemed impo various modeling groups or if the categories are redundant. In the ca excluded elements, blank spaces have been added to the table which can filled with new descriptors. Redundancy is expected and encouraged in der to provide a check on the completeness of the descriptions and to ver different interpretations of various categories.

Five significant problems could be encountered in the application of itial test cases:

- Model inputs may differ from proposed initial test case inputs
- Model outputs may differ from required test case outputs
- Model components (i.e., pool spread, evaporation, gravity cloud spread, dispersion) may not be completely separable
- A model may not include a particular component effect or test case parameter
- Component analysis results in a large number of test cases.

The first two questions of model inputs and outputs may require mino dification of some LNG models to provide for intermediate inputs and ou review of model descriptions in the literature provided inputs and outp st common to existing models. A great diversity of model objectives an dels made this formulation difficult.

is incorporated into models as either a density intrusion resulting in a separate calculation for maximum radius due to gravity spread or as a com nent of dispersion parameter estimates as a part of the dispersion compo In these situations, the extreme ranges of variables in the test cases a partial comparison of separate models and models with combined nonsepara effects. The latter models should use only the test cases for the domin component of the combination. For example, a mixed gravity spread/dispe model would use dispersion test cases, since the dispersion model test c both include all spill information inputs needed and demonstrate the sam put (maximum distance to lower flammability limit) as the mixed model.

Models not having components should ignore test cases for those com nents. Models missing parameters should reduce the number of test cases to eliminate tests showing the variability of the missing variable. For example in the vapor dispersion tests (Table 13) the four parameter Box-Behnken design would be reduced from 25 cases to 13 cases with the remov of heat addition to the vapor cloud. An explanation of the variations i the test cases due to changing numbers of parameters is presented in the appendix.

The number of test cases presented is largely due to the requiremen the response surface designs used with component breakdown of the model. It is not expected that this will be significant in practice since the analyses of components in most cases represent single equations in the m and will not require calculations through the whole model code.

REFERENCES

1. American Gas Association, LNG Safety Program. Phase III, Conseque of LNG Spills on Land. AGA-IS-3-1, 1973.

2. Boyle, G. J., and A. Kneebone, Laboratory Investigations into the Characteristics of LNG Spills on Water. Evaporation, Spreading, a Vapor Dispersion. Shell Research Limited, Thornton Research Cente Chester, UK, March 1973.

3. Havens, J. A., Predictability of LNG Vapor Dispersion from Catastr Spills onto Water: An Assessment. U.S. Coast Guard, Washington, April 1977.

4. The Japan Gas Association, A Study of Dispersion of Evaporated Gas Ignition of LNG Pool Resulted from Continuous Spillage of LNG Cond During 1975. April 1976.

5. Reid, R. C., R. Wang, "The Boiling Rates of LNG on Typical Dike Fl Materials." Cryogenics, 18(7):401-404, July 1978.

6. Strategy of Experimentation, Applied Technology Division, E. J. Du de Nemours and Co., Inc., Wilmington, Delaware, October 1975.

MODIFICATION OF TEST CASES NECESSITATED BY REDUCED NUMBERS OF PARAMETERS

The test cases presented in the report assume that the effects of th four parameters will be simulated in each of the four components of LN por generation and dispersion models. All models are not structured to cept all the parameters since the models have been developed for differ plications or have been developed based on different sets of assumption is appendix explains the structure of the 3 and 4 parameter Box-Behnken perimental design so that modifications to proposed test cases can easi implemented in situations where models cannot simulate the effects of l parameters.

As stated in Section 3, the Box-Behnken designs are a means of syste cally defining the response of a dependent variable to changes in one o re independent variables. The designs allow identification of response rfaces with parameter interactions and single parameter effects with a nimum number of tests. The designs make use of inputs in the form of ximum, midpoint and minimum values in a parameter range. The three and ur parameter test cases presented in Section 3.0 consist of combination these three numbers with appropriate magnitudes determined for each of e four listed components of LNG vapor generation and dispersion.

The generalized form of the three and four parameter Box-Behnken des n be seen in Tables A.1 and A.2. In the tables, the midpoints are signated by a symbol "0", the range maximum is given by "+", and the nge minimum is given "-". The parameters, x_i, can be specified in any t the order must be carried completely through testing.

The confusion in use of this analysis technique on a group of models at some models may not have complete parameterizations in terms of the sted test cases. This problem can be overcome by using design of fewer rameters. For example, Table 13 provides test cases using four paramet nd speed, atmospheric stability, spill radius and heat addition to the

Test No.	x_1	x_2	x_3
1	+	+	0
2	+	-	0
3	-	+	0
4	-	-	0
5	+	0	+
6	+	0	-
7	-	0	+
8	-	0	-
9	0	+	+
10	0	+	-
11	0	-	+
12	0	-	-
13	0	0	0

TABLE A.2. Four Parameter Box-Behnken Design

Test No.	x_1	x_2	x_3	x_4
1	+	+	0	0
2	+	-	0	0
3	-	+	0	0
4	-	-	0	0
5	0	0	+	+
6	0	0	+	-
7	0	0	-	+
8	0	0	-	-
9	+	0	0	+
10	+	0	0	-
11	-	0	0	+
12	-	0	0	-
13	0	+	+	0
14	0	+	-	0
15	0	-	+	0
16	0	-	-	0
17	+	0	+	0
18	+	0	-	0
19	-	0	+	0
20	-	0	-	0
21	0	+	0	+
22	0	+	0	-
23	0	-	0	+
24	0	-	0	-
25	0	0	0	0

r design as shown in Table A.1 should be used and the deleted variable e ignored or given the constant value from Table 14. If only one or neters can be identified in a model, the designs of Tables A.3 and ld be used.

TABLE A.3. One Parameter Tests

Test No.	x_1
1	+
2	-
3	0

TABLE A.4. Two Parameter Tests

Test No.	x_1	x_2
1	+	+
2	+	-
3	-	+
4	-	-
5	0	0

REPORT D

Radiation from Burning Hydrocarbon Clouds

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Prepared for the
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U.S. Department of Energy
under Contract EE-77-S-02-4204

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TABLE OF CONTENTS

FIGURES

TABLES

SUMMARY

This paper reports on the measurement and analysis of time resolved thermal radiation from combustion of methane, ethane, and pr clouds formed from laboratory scale vapor samples initially contained a soap bubble. The time scale of the radiant heat pulse was found to the same as that of the fluid mechanical motion (Fay and Lewis, 1976) time-integrated radiant energy flux, expressed as a fraction of the i fuel heating value, was between 0.09 and 0.15 for these fuels, with s dependence on initial fuel volume. The radiation was correlated by a gas model, which assumed a uniform time-dependent temperature in a sp cloud and a time-independent absorption coefficient. The grey gas te ture decreased monotonically during and after the period of combustio absorption coefficient was found to be a function of the initial fuel and fuel type; it was between 10^{-3} and 10^{-2} cm^{-1} and decreased slight increasing initial fuel volume.

INTRODUCTION

The combustion of a cloud of pure fuel vapor (or a very ri vapor/air mixture) initially unconfined in still air can occur as an unsteady turbulent diffusion flame (Fay and Lewis, 1976). When the c is first ignited at its edge, the buoyant product gases begin to rise mixing surrounding air with the unburned fuel and thus continuing combustion until all the fuel is consumed. During the period of comb tion, the luminous burning gas volume increases in size and altitude until the flame is finally extinguished for lack of fuel. Such a flan is the unsteady analog of the buoyancy dominated diffusion flame forme above a steady jet of fuel vapor having negligible initial momentum (Thomas, 1963).

The volume of combustion gases formed during this type of unsteady diffusive burning has been termed a "fireball" (Gayle and Bransford, 1965). It has been most commonly observed in sudden accide releases of rocket propellants (Gayle and Bransford, 1965, and Bader, et. al., 1971) and liquid propane (National Transportation Safety Boarc 1972). Large amounts of fuel vapor can be formed after accidental spi of cryogenic fuels on water or land and could possibly be ignited and burned in this manner (Fay and Lewis, 1976).

Even though vapor clouds burn rapidly, no significant over-pr results from this mode of combustion. However, thermal radiation from burning gases may be intense enough to be hazardous (Hardee et. al., 19 The burning time of large fireballs is less than ten seconds (Gayle and

Bransford 1965), and hence the duration of the radiant heat pulse is comparable to that of a nuclear explosion (Hardee and Lee, 1971). Since the response of humans to thermal radiation from flames depends upon both the intensity and duration of exposure (Buettner, 1951), the radiative characteristic of fireballs which is of interest in hazard analysis is the intensity as a function of time.

In the absence of a detailed experimental study, such as this paper describes, it might be expected that the instantaneous value of radiant intensity would depend upon the instantaneous volume and shape of the luminous combustion products in the same manner as for a steady (on average) jet diffusion flame, and that the intensity variation with time will follow (although not proportionally so) the growth and then decay of the fireball volume and surface area. We have used this hypothesis to describe our experimental results and to correlate them with a grey gas model. As will be seen below, such a description can be cast in a nearly dimensionless form which may be suitable for extrapolation to larger flame sizes than could be accomodated in our laboratory.

It is usually supposed that the combustion in a turbulent diffu flame occurs at the interface between eddies of air and fuel brought into contact by the entrainment action of the large scale energy-containing eddies and that the chemical reaction proceeds in a manner similar to that in a laminar diffusion flame. Of course, the time and length scales of combustion reaction zone are not known in detail; the macroscopic time a

(1970) and Markstein (1976a, 1976b) are known. Thus the thermodynamic s within the flame is believed to be exceedingly inhomogeneous. Neverthel grey gas models have been used successfully to correlate the radiative characteristics of steady turbulent diffusion flames (Markstein, 1976a).

Thermal radiation from turbulent diffusion flames of hydrocarb vapors is emitted and absorbed by carbon particles and molecular product of combustion (mainly water vapor and carbon dioxide) although the latte may account for only a small portion of the radiation from laboratory sc flames (Felske and Tien, 1973). The total thermal flux reaching a recep outside the flame is thus affected by the distributions of radiating and absorbing species and gas temperature within the flame. In the present experiments, it is also time dependent. The measurements to be reported were resolved in time (but not in space or wavelength) an thus represent the first effort at deciphering the thermal radiation pu from these flames.

Spatially resolved measurements of both radiance and absorptance of steady turbulent flames (Markstein 1976a, 1976b) make it possible to determine the parameters (absorption coefficient and radiance temperature) used to correlate data by a grey gas model. Because of experimental limitations, only total flame radiance could be measured (as a function of time) in our experiments, and thus a grey ga model can only establish a relationship between the model parameters. analysis discusses this relationship and compares the range of these parameters with literature values derived from steady flame measurement

Observation and analysis of the motion of a burning vapor cl
reported by Fay and Lewis (1976), showed that the time to complete com
as measured by the duration of visible light, is proportional to $g^{-1/2}$
(where V_f is the initial fuel vapor volume and g is the acceleration o
gravity) and that the maximum height and diameter of the flame are pro
tional to $V_f^{1/3}$. The dimensionless proportionality constants were fou
be different for each fuel tested (methane, ethane and propane) but no
greatly so (Lewis 1977). A detailed entrainment model was also propos
to explain the growth with time of the burning cloud. It was based up
hypothesis that the fuel vapor burned at a rate proportional to the ra
entrainment of surrounding air. This model, which in effect hypothesi
invariant thermodynamic state within the fireball during the process o
combustion, necessarily conforms to these same scaling laws. However,
be seen below that the detailed observations of fireball growth disagr
the Fay and Lewis (1976) dynamical model, even though the overall comb
time, fireball size, and height vary according to these dimensionally
and simple laws. We conclude that these observations imply a decreasi
temperature within the fireball; this is also consistent with deductio
the grey gas model.

Compared to steady turbulent flames, fireballs are dynamical
complex, and their radiative properties are more difficult to categori
this paper we correlate the overall radiative properties for laborator
fireballs in a way which is consistent with the dynamical scaling laws
previously shown. In addition, by a grey gas model, it is possible to

the radiation temperature history in the fireball when plausible assumpt are made regarding the absorption coefficient. Observations and model m be used together to extrapolate radiative properties of fireballs to som larger sizes.

This grey gas model (and the series of experiments which are correlated by it) is more extensive than that reported by Hardee et al. (who use a black or grey gas model with a time-invariant thermodynamic sta o predict the thermal pulse from fireballs formed from both premixed and nmixed methane samples. It will be seen below that our results, which a irectly applicable to small, laboratory scale experiments, are not incons ith the few observations and predictions of Hardee, et. al., for much larg izes. On the other hand, it will also be seen that there exists some amb the interpretation of any limited set of experiments of the type we hav nducted, so that it is not at all certain how to extrapolate to extreme rge sizes.

An experimental program was undertaken (Lewis, 1977) to measure
he motion, growth, and thermal radiation from a fireball formed by igniti
f a vapor sample initially confined within a spherical soap film. By to
t with a hot wire, the film was broken and the combustion was initiated.
or each of three fuel types (methane, ethane, and propane), tests were
onducted over a range of initial fuel volumes from ~ 20 cm^3 to ~ 200 cm^3

The motion and growth of the fireball were recorded with a high
peed camera. The horizontal diameter and highest point of the visible
lame were measured from the film as a function of time since ignition (F
nd Lewis, 1976). The gas burned as an unsteady turbulent diffusion flam
nd at times during combustion the flame was irregularly shaped. Because
he irregular shape, the measured diameter was defined as that of a circl
hose area equalled the projected area of the flame as viewed by the came

The thermal radiation from the fireball was sensed by a broad b
adiation detector. The detector was equipped with a barium fluoride wi
hich had a constant transmissivity of 0.95 over the wavelength range of
.16 to 16 microns. The output of the detector (response voltage as a
unction of time) was recorded on an oscilloscope. The linear response
oltage vs. incident radiant flux characteristic and the first order tra
ent response of the detector were verified experimentally in a calibrat
xperiment (Lewis 1977) and were used in subsequent data reduction. The
ngle within which the detector viewed the fireball did not exceed 13^0 s
s to minimize any angular dependence of the relative response. The dis
f the detector from the fireball was initially adjusted in proportion t
xpected maximum flame diameter (which varies as the cube root of the in
uel volume) so as to maintain geometric optical similarity.

IREBALL DIAMETER AS A FUNCTION OF TIME

In the analysis which is to follow, the radiation measurements w
e compared to a grey gas model to deduce a mean fireball temperature as a
unction of time. In order to apply this spherically symmetric grey gas
del, the diameter D of the fireball, averaged over several repeated expe
nts, must be known as a function of time.

The experiments for determining the temporal growth of the fireb
ich were conducted for methane, ethane, and propane, were performed over
nge of initial fuel volumes V_f. To correlate the results in a convenient
rm, the measurements of fireball diameter and time were nondimensionalize
th respect to initial fuel volume by the following relations, which confo
the dynamical scaling law of Fay and Lewis (1976):

$$\delta \equiv D/V_f^{1/3} \quad (1$$

$$\eta \equiv t\, g^{1/2}/V_f^{1/6} \quad (2)$$

re t is the real time since ignition. The dimensionless diameter δ of
visible flame as a function of the dimensionless time η, when plotted
og-log paper, could be fitted by a straight line. (An example is shown
ig. 1.) Thus it was found that the average dimensionless diameter of
fireball as a function of time could be expressed empirically as

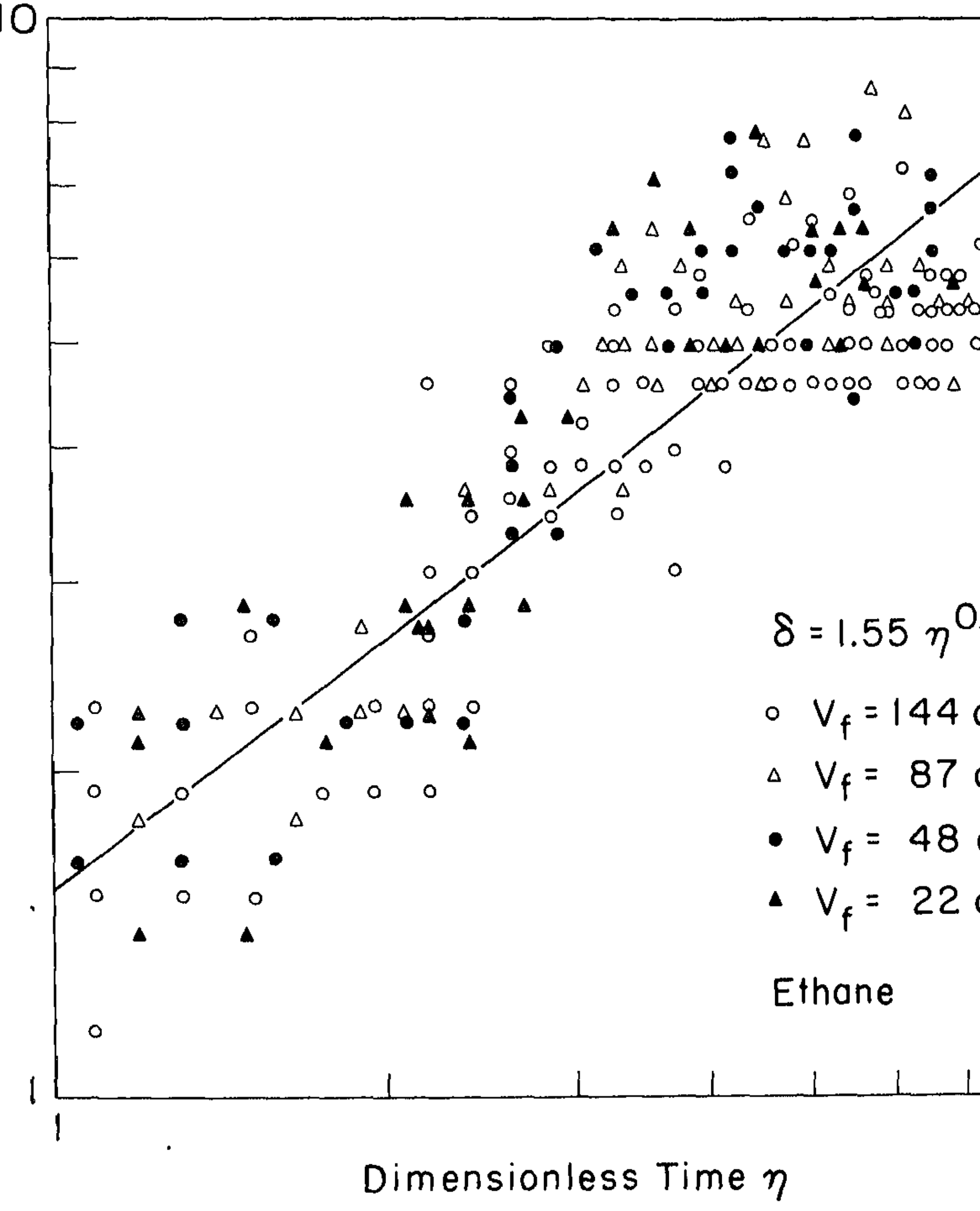

Fig. 1 Dimensionless Fireball Diameter as a Function of Dimensi
Time for Ethane. (Data points fitted by a straight line
log-log paper.)

The number in parentheses following each fuel type is the standard geom
deviation of the data from the empirical curve.

Table I: Constants for Determining Dimensionless Diameter as a Function of Dimensionless Time (Eq. 3)

	α	β
Methane (0.69)	1.15	0.84
Ethane (1.02)	1.55	0.77
Propane (1.05)	0.81	1.12

The Standard Geometric Deviation is Listed in Parentheses

The empirical relation just described, which related firebal diameter as a function of time, was deduced from measurements of the projected area of the visible flame. The flame was visible for a dime time η less than about 9. Beyond this time, the increase of diameter

ustion products cannot be determined from the photographic technique u
s clear that the cooling, rising fireball must grow in size after the
me ceases to be visible. Furthermore, some radiation was still detecta
er visible luminosity had ceased. To compare the observed radiation in
s post-luminous period with the grey gas model, it was necessary to ext
ate the growth law of Eq. (3) to somewhat later times than $\eta = 9$. To
stify such an extrapolation, a buoyant thermal model (Morton, et. al.,
the fireball products was constructed. This model should be valid fo
mes long compared with the burning time. The dimensionless diameter as
function of dimensionless time would then be governed by the empirical
r small times and by the buoyant thermal model for large times. The di
ess time at which the functional dependence changes was found to be $\eta \sim$
ethane and ethane and $\eta \sim 12$ for propane. For this reason an extrapola
f the empirical diameter relation of Eq. (3) to a dimensionless time η
or use in the grey gas model during the post luminous period of $9 < \eta <$
eems reasonable.

The empirically observed growth law for fireball diameter (Eq
shows a slower growth rate than the theoretical entrainment model of Fa
Lewis (1976) for which $\beta = 2$ (rather than the values near unity shown i
Table I). This difference can be ascribed to the inconstancy of the pr
gas density which Fay and Lewis assumed to be invariant during the comb
process. To illustrate the consequences of this distinction, we consi
the model equation for vertical motion as given by Fay and Lewis:

$$\frac{d}{dt}\left[\frac{\pi D^3}{6}\rho_p \left(\frac{dz}{dt}\right)\right] = \frac{\pi D^3}{6} g (\rho_a - \rho_p)$$

in which ρ_p and ρ_a are the product gas and air densities resp
is the elevation of the fireball above its initial position.
side of Eq. (4) is the rate of change of vertical momentum of
and the right hand side is the buoyant force acting upon it.)
and z are observed to vary as simple powers of t (Lewis 1977)
that

$$\frac{\rho_a}{\rho_p} - 1 \simeq \frac{T_p - T_a}{T_a} \sim t^{\gamma-2}$$

where $\gamma = d(\ell n\, z)/d(\ell n\, t)$ and T_p and T_a are the product gas anc
atures respectively. For propane, Lewis (1977) found $\gamma = 0.86$
that the product gas temperature excess above atmospheric leve
as the - 1.14 power of t or η. As will be seen below, the grey
evidence of a declining temperature during the period of combus

It would seem to be difficult to model the apparently
thermodynamic state within the burning fireball. The hypothesi
and Lewis that each increment of entrained air is instantaneous
burned with a matching (but non-stoichiometric) increment of fu
is at variance with the observed motion. Given the observed ri
the fireball and the duration of combustion, there is barely tin
gas inside the fireball to circulate more than once or twice bef
is complete. Indeed, it is remarkable that the fuel is burned s
within such a short distance of travel. Because the inhomogenei
great, it is perhaps not so surprising, in retrospect, that the
model of Fay and Lewis is not supported by the observations.

Despite the failure of the detailed entrainment model to predic
e growth of diameter correctly, the overall relation of combustion time
d maximum fireball diameter to initial fuel volume are correctly modell
the observations of Fay and Lewis (1977) clearly show. This implies
at the thermodynamic state of the fireball, while not invariant during
mbustion, must be a function of the dimensionless time η as implied
Eqs. (4) and (5). It is primarily for this reason that the subsequent
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e explicit dependence upon the variables and initial conditions can be
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Despite the failure of the detailed entrainment model to predic the growth of diameter correctly, the overall relation of combustion time and maximum fireball diameter to initial fuel volume are correctly modell as the observations of Fay and Lewis (1977) clearly show. This implies that the thermodynamic state of the fireball, while not invariant during combustion, must be a function of the dimensionless time η as implied by Eqs. (4) and (5). It is primarily for this reason that the subsequent analysis of the thermal radiation is cast in a dimensionless form so tha the explicit dependence upon the variables and initial conditions can be minimized.

REDUCTION OF RADIATION MEASUREMENTS

The grey gas model, which will be applied later, has dependence upon fireball diameter in the limiting cases of lar absorption coefficient. If the fireball is a blackbody, the r heat emission is proportional to the surface area of the fireb Alternatively, if the fireball is transparent, the radiant hea proportional to the volume of the fireball. The method of exp radiation measurements in a nondimensional form should be cor with the grey gas model.

To reduce the radiation measurements to a dimensionl us suppose that the integrated radiant heat pulse is a small f total fuel heating value available in the initial charge. We fraction to be insensitive to initial fuel volume. Noting tha of the burning process is proportional to $g^{-1/2}\ V_f^{\ 1/6}$, we can dimensionless total radiant heat emission rate ν by:

$$\nu\ \{\eta\} \equiv \frac{(q_d)\ (4\pi r^2)}{g^{1/2}\ \rho_f\ h_f\ V_f^{\ 5/6}}$$

where q_d is the radiant heat transfer rate per unit area measu detector, and r is the distance from the center of the firebal detector; they are both functions of the dimensionless time η. enthalpy of combustion, and initial volume of fuel are ρ_f, h_f, respectively. If the radiation from the fireball was isotrop integral of the dimensionless radiant heat emission rate with time would be the ratio of the heat radiated to the total fuel

However, since the radiation is not necessarily isotropic, ν is a dimensionless measure of the radiation predominantly in the equatorial plane.

In analyzing the data, it was found for each fuel type that the peak of the radiant heat transfer pulse occurred at a value of η which was independent of fuel volume, but the pulse integral was a slowly varying function of the initial fuel volume. Thus, the ratio of heat radiated to the total fuel heating value varied with the initial fuel volume. To correlate this dependency, the dimensionless heat transfer rate ν was normalized by dividing it by its integral:

$$\bar{\nu} = \nu / f$$

where

$$f \equiv \int_0^\infty \nu d\eta$$

Thus defining a new normalized rate $\bar{\nu}$. It was found that the value of f as a function of initial fuel volume could be correlated by:

$$f = B\, V_f^{\,C}$$

where the dimensionless constants B and C are given in Table II for the fuel types. Note that the low values of C indicate a weak dependence of the dimensionless radiant heat pulse on initial fuel volume.

Table II: Constants for Determining f

	B	C
Methane	0.204	-0.180
Ethane	0.116	0.000
Propane	0.095	0.113

Using the correlation of Eq. (8), the average valu
the range of initial volumes tested were about 0.09, 0.12, a
methane, ethane, and propane respectively. Assuming isotrop
f would then be the fraction of fuel heat which is lost by r
the combustion of the initial sample. For steady turbulent
(1976a) has found f to be 0.20 to 0.24 for propane. Thus o
ments indicate that the radiant heat loss, expressed as a fr
heat, is not greatly different from that for steady flames.

The normalized dimensionless heat transfer rate $\overline{\nu}$
as a function of η for each test, and an average value for e
deduced by smoothing out the data from the individual tests.
this was done by taking the integral of Eq. (7), finding the
of that integral at a specific time, and finally measuring t
average integral curve at several locations. The values of
are shown in Fig. 2.

The normalized dimensionless heat transfer rate $\bar{\nu}$ shown in Fig. ows some dependence upon fuel type. The peak intensity occurs at a some at earlier time (η = 4.5) for methane than for ethane and propane (η = 6 is seems to indicate a more rapid buildup of soot in the methane flame. is also noticeable that measurable (although small) radiation occurs af e disappearance of visible luminosity, which occurs at η = 8.5 for metha d propane and 10.6 for ethane (Lewis 1977).

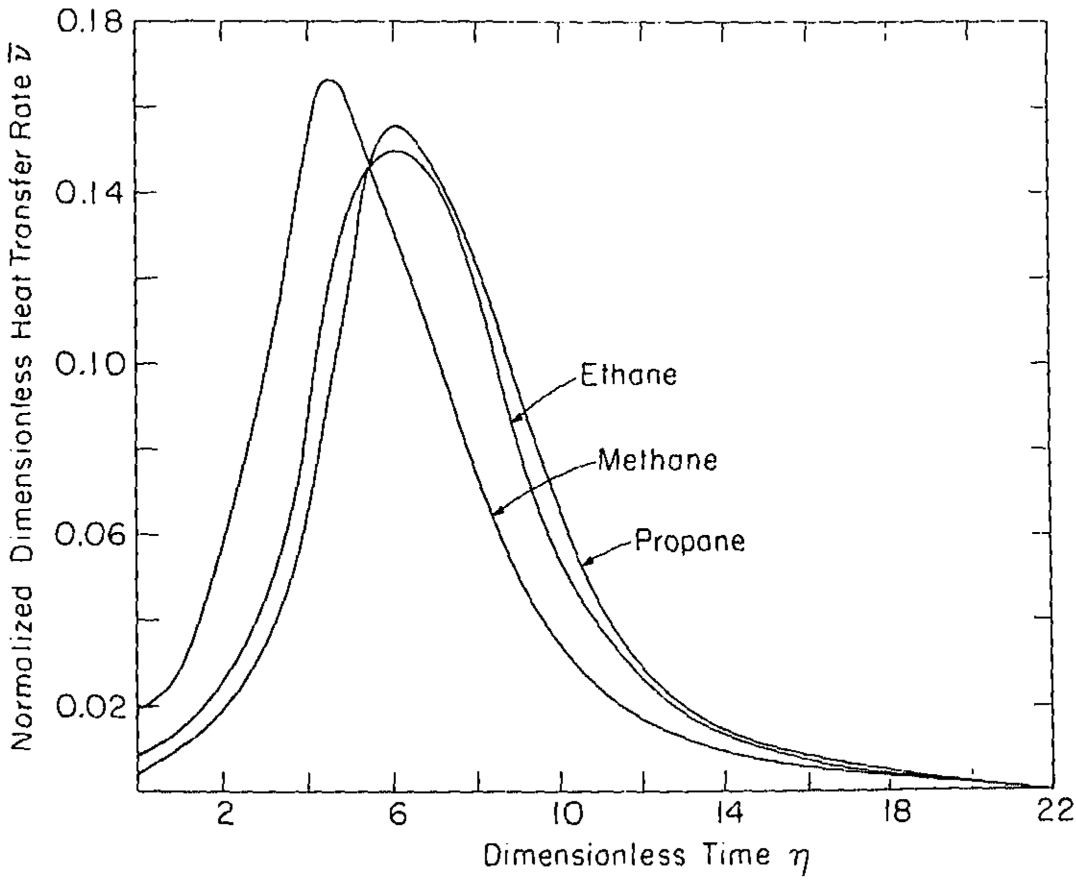


Fig. 2 Normalized Dimensionless Heat Transfer Rate as a function of Dimensionless Time for methane, ethane, and propane. Average curves deduced from several tests over a range of initial fuel volumes.

To help provide a basis for understanding the observed radiation from the experimental fireballs, we propose to model the fireball as a spatially uniform grey gas. We assume that the combustion gases, at any moment, are uniform in temperature within a spherical volume whose diamete D is equal to the observed average diameter of the visible flame appropria to the time t since combustion began. The grey gas absorption coefficient is assumed to be constant during the combustion process, but the uniform temperature T_f will be assumed to vary with time t. This variation will be determined by equating the measured radiant flux with that calculated from this grey gas model.

These assumptions concerning K and T_f are simplifying ones. Wh it is very likely that both K and T_f vary with time and position within th fireball, the grey gas model will define a spatial average of K and T_f wh can then be examined for temporal dependence as evidenced by the measured radiation. We expect that the major time dependence of the radiation wou be governed by changing temperature and, for simplicity, assume that K is constant during the period of measurable radiation. (As will be explaine below, we consider that K may depend upon the initial fuel volume which d mines combustion duration).

The direct radiative flux from a grey isothermal volume can be expressed as the product of a geometrical factor, which accounts for the and absorptivity of the volume, and the emissive power of a blackbody at the temperature of the enclosed medium (Hottel and Sarofim, 1967). For a

spherical volume of grey gas, the radiative flux q_d received by the detector at a distance r from the center of the fireball is given by

$$q_d = \left[1 - \frac{2}{K^2D^2}\left\{1 - (1 + KD)e^{-KD}\right\}\right]\left[\sigma(T_f{}^4 - T_a{}^4)\right]\frac{D^2}{4r^2}$$

where σ is the Stefan-Boltzmann constant, and T_a is the atmospheric temperature. The latter is included in this equation because the dete measures radiation above the blackbody background level.

Since we have assumed that the major time dependence of the radiation is the result of changing temperature, Eq. (9) will be solv the uniform temperature T_f as a function of the dimensionless time η diameter D is given by Eqs. (1) and (3) and the radiant heat transfer the detector q_d is determined from Eqs. (6), (7), and (8) together wi Fig. 2. Thus

$$T_f \doteq \left[\frac{q_d\ 4r^2}{\sigma\ D^2\left[1 - \frac{2}{K^2D^2}\left\{1 - (1 + KD)\ e^{-KD}\right\}\right]} + T_a{}^4\right]^{1/4}$$

Except for the effects of radiative heat loss, we expect th temperature T_f to depend only upon the dimensionless time η and not upon the initial fuel volume so as to preserve the thermodynamic However, it can be seen from Eq. (10) that $T_f\{\eta\}$ depends upon V_f as parameter through the terms q_d, D, and possibly K. As a first trial,

ticed that by a suitable choice of K (different for each fuel but indepe
nt of fuel volume) the temperature histories for all fuel volumes, for a
rticular fuel type, were nearly identical. Except for methane, the
lues of K determined in this way were not greatly different from publish
lues (Yuen and Tien, 1976) for laminar diffusion flames of these fuels a
own in Table III.

Table III: Comparison of Absorption Coefficients and Grey Gas Temperatures

	(K^*)	$(K^\dagger)$	(T_f^*)	$(T_m^{\dagger\dagger})$
	cm^{-1}		°K	
Methane	1.0	0.0645	630	1289
Ethane	0.155	0.0639	640	1590
Propane	0.115	0.1332	790	1561

* K and T_f at time of maximum radiation determined from Eq. (1

† Listed values of soot emission parameter by Yuen and Tien (1

†† Listed values of the mean flame temperature by Yuen and Tien

By this method of analysis, the temperature T_f declined monoto
with n, but the temperature at the time of maximum radiation was only a
600-800°K. This is substantially lower than the mean flame temperature
between 1300-1600°K listed by Yuen and Tien for these fuels as shown in
Table III. The grey gas radiation temperature for turbulent flames of
and propane measured by Markstein (1976a) are also close to those liste
Yuen and Tien. Thus the assumption that K could be considered a const
was abandoned because of the unrealistic temperatures which were inferr
from this grey gas model.

It is expected that during combustion the uniform temperature
should be approximately the same as the mean flame temperatures of Yuen
and Tien shown in Table III. Furthermore, since the absorptivity is a
function of the carbon particle density, it may be that K should be con
ered a function of the initial fuel volume, which determines the combus
time and thus might affect the amount of soot formed. By setting the u
temperature at the time of peak radiation equal to this mean flame temp
Eq. (10) was solved for K as a function of the initial fuel volume. K
found to decrease slightly with increased fuel volumes and is shown in

The values of K shown in Fig. 3 are smaller by a factor of 10
than the values listed in column 2 of Table III for steady flames of sm
dimensions but large optical depth. It seems reasonable that the turbu
unsteady fireball will have a smaller volume fraction of reacting, radi
gas than the flames from which the column 2 values were measured. Thus

existing data. Furthermore, Brown, et. al., (1974) deduced a value of $K = 1.8 \times 10^{-3}\ cm^{-1}$ for LNG pool fires of 6 to 80 ft. diameter, which is consistent with Fig. 3.

The gradual decline of K with increasing initial fuel volume as shown in Fig. 3 could be interpreted as a reduction in soot concentration as the combustion time increases. Presumably, soot burn up occurs earlie in the combustion period for the larger initial volumes.

The uniform temperature as a function of time was calculated fo a range of fuel volumes using these values of K. By assumption, the temp ture at the time of peak radiation determined in this way is equal to the flame temperature in column 4 of Table III. It was found that the temper history as a function of η was practically identical for all fuel volumes hence preserving thermodynamic similarity. These temperature histories a shown in Fig. 4 as solid lines.

It can be seen from Fig. 4 that the temperature declines monoto during the period of radiant heat emission. This decline is initially sl until luminosity ceases ($\eta \sim 8$), and subsequently quite rapid. The initia gradual decline of temperature is consistent with the interpretation of dynamics of the fireball given by Eq. (5).

It is possible to compare these inferred uniform temperature histories with the thermodynamic temperature whose upper limit is contro by the heat released in combustion. This thermodynamic temperature limi is determined by equating the fireball enthalpy for any diameter to the available fuel heating value to give:

$$T_t = T_a \left[1 - \frac{6 \rho_f h_f V_f}{\rho_a c_p T_a \pi D^3} \right]^{-1} \qquad (11)$$

re ρ_a, T_a, and c_p are the density, absolute temperature, and specific the surrounding air. Of course, Eq. (11) is not valid for values of T_t ch exceed the adiabatic flame temperature.

The thermodynamic temperature limit T_t as a function of time is o shown in Fig. 4 as a dashed line. The curves for the uniform grey and the thermodynamic temperatures cross at the dimensionless time η between 7-8 in all cases. This corresponds to about the time at which visible flame disappears.

Figure 4 indicates that the radiation temperature is somewhat her during the declining phase of radiant heating than is permitted by hermodynamic energy balance. We do not consider this discrepancy to significant in view of the assumptions of the grey gas model regarding formity of temperature and absorption coefficient. What is significant ut the comparison is the rapid decline of temperature, which occurs at ate which is consonant with the thermodynamic calculation.

Hardee, et.al. (1978) conducted combustion experiments on pure hane samples (initially enclosed in a plastic bag) which burned in the eball mode. Their initial fuel volumes, between 1.5×10^5 and 1.5×10 , were 5×10^2 to 6×10^4 times as large as the largest samples tested the experiments described above. Integrated heat transfer per unit a of gage surface was reported for gages located near the center or

face of the fireball. These measurements are not directly comparable
ours where the radiation detector was located at a distance from the
eball and measured the instantaneous heat transfer rate as a function
time.

Despite these differences in initial fuel volume and measureme
chnique, for comparison, we extrapolated our grey gas model to the
ch larger sizes and integrated the heat flux per unit area of flame
rface over the time period of measurable radiation. The predictions o
grey gas model, extrapolated to these much larger sizes, were found
only 10-20% of the measured values of Hardee, et.al. (1978). However
ch an extrapolation, which assumes that the absorption coefficient K
ntinues to decline with increasing initial fuel volume beyond the valu
own in Fig. (3), is not justifiable.

Instead, we used the observations of Hardee, et.al. (1978) to
termine a value of K at these large initial fuel volumes which brought
eir measurements and our grey gas model into agreement. On this basis
have determined that a value of about 7×10^{-4} cm^{-1} for K used in the
ey gas model would result in predictions which are consistent with the
asurements of Hardee, et.al. Thus the decline in absorption coefficie
with increasing initial fuel volume V_f shown in Fig. 3 probably levels
f to such a value for methane for these large initial fuel volumes.

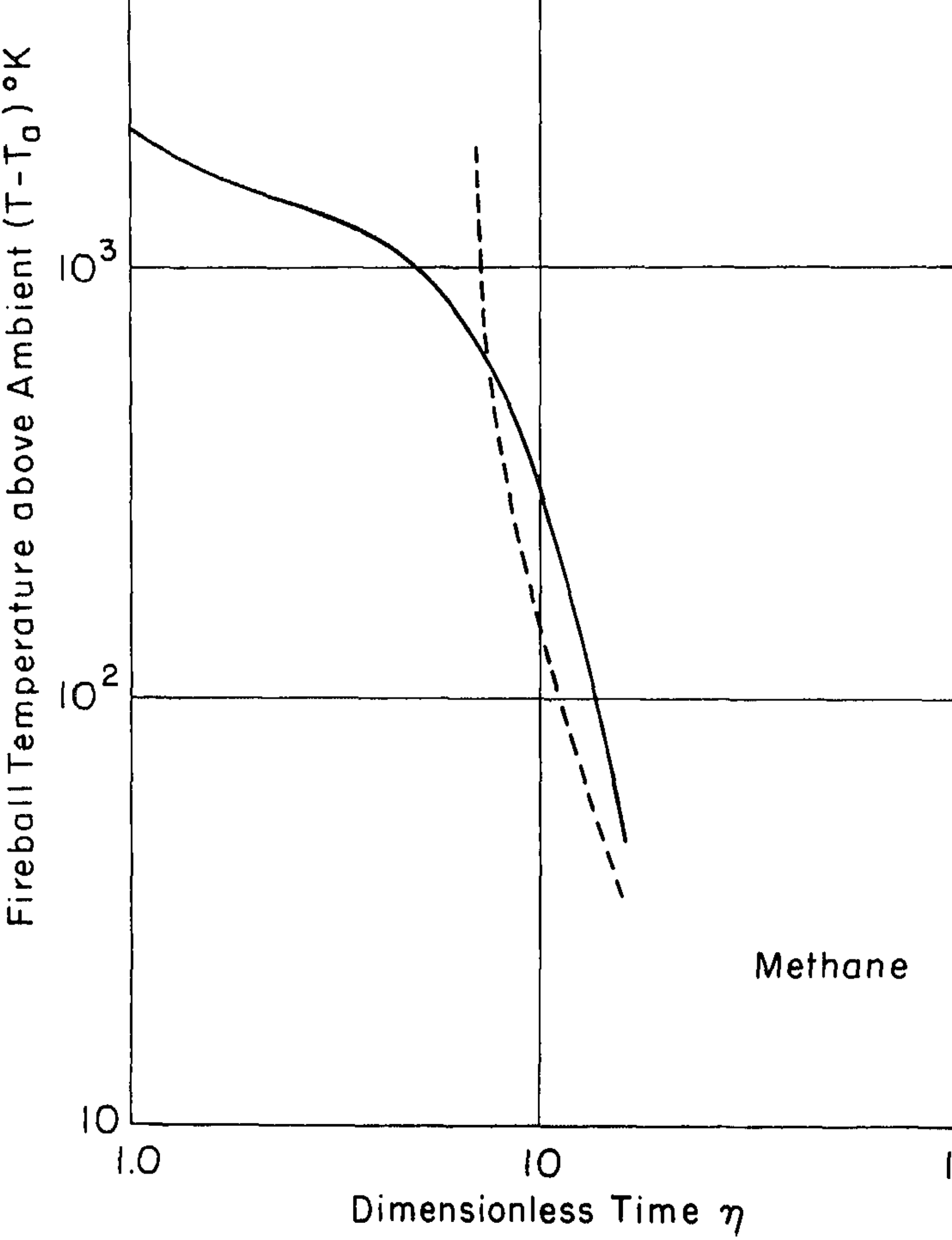


Fig. 4(a) Fireball Temperature as a function of Dimensionless Time methane. (The solid line represents the uniform temperatu inferred from the grey gas model, and the borken line rep the thermodynamic temperature controlled by the heat rele combustion. The thermodynamic temperature does not excee adiabatic flame temperature.)

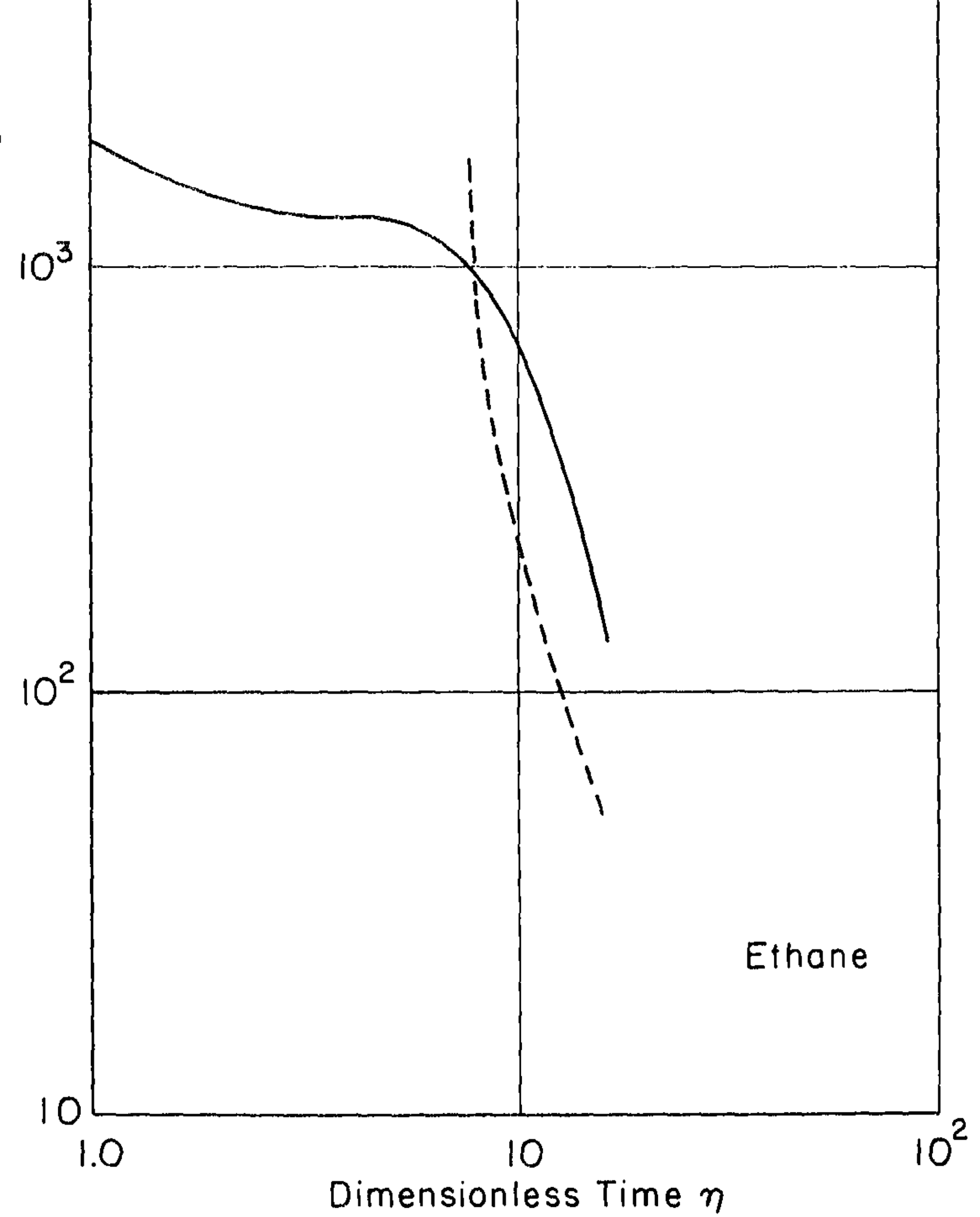
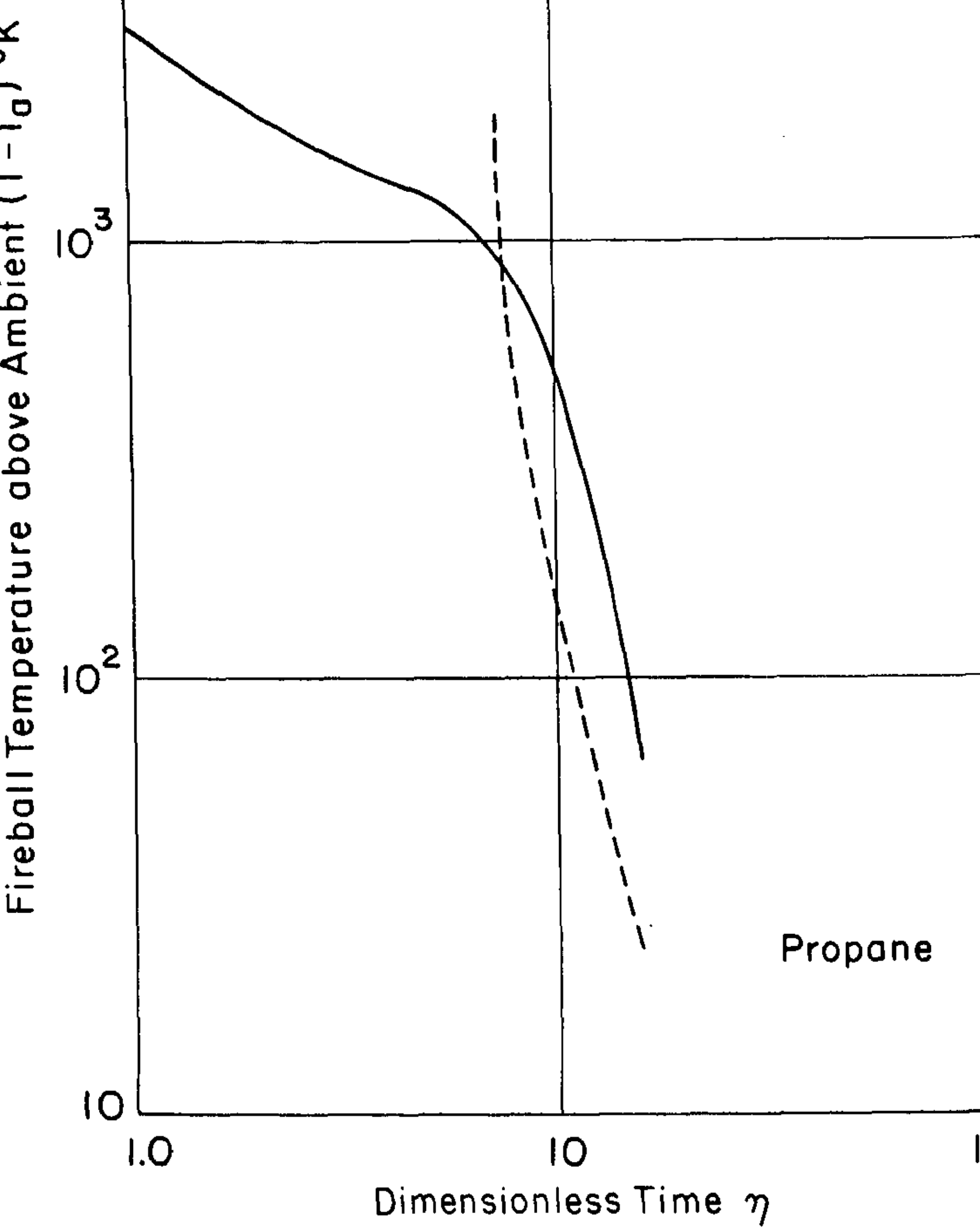


Fig. 4(b) Fireball Temperature as a function of Dimensionless Time for ethane. (The solid line represents the uniform temperature inferred from the grey gas model, and the broken line repres the thermodynamic temperature controlled by the heat release combustion. The thermodynamic temperature does not exceed f adiabatic flame temperature.)



(c) Fireball Temperature as a function of Dimensionless Time fo
propane. (The solid line represents the uniform temperature
inferred from the grey gas model, and the broken line repre
the thermodynamic temperature controlled by the heat releas
combustion. The thermodynamic temperature does not exceed
adiabatic flame temperature.)

JSIONS

The time integrated heat flux is a measure of the total thermal tion from the fireball, and it can be expressed as a fraction of the fuel ng value. It was found that this fraction was nearly independent of nitial fuel volume. For methane it averaged about 9% and decreased increased fuel volume, was constant for ethane at 12%, and for propane eraged about 15%, increasing with increased fuel volume. These results onsistent with measurements on steady flames.

The duration of the radiative pulse was found to scale with initia volume as $g^{-1/2}\ V_f^{\ 1/6}$, which is identical to the scaling law for visibl height previously observed by Fay and Lewis (1976). Such a scaling s consonant with the hypothesis that the fluid mechanical motion, which minated by gravitational forces, determines the duration of the evolu- of the thermodynamic state of the reacting gas.

The observed radiation histories could be explained by a grey gas which assumed uniform (but time dependent) temperature within a spheri loud and a time independent absorption coefficient. In such a comparis ireball growth, which scaled in time according to the fluid mechanical ng law, was empirically determined from observations of visible luminos it was assumed that the absorption coefficient was independent of initi volume, but had a value which reduced the grey gas temperature to a func of the dimensionless time only, the inferred temperatures were well bel ved flame radiation temperatures in steady flames. This assumption was rded as unrealistic. Instead, the absorption coefficient was determine function of initial fuel volume by requiring that the flame temperature

at peak radiant intensity be the same as that measured in steady flames. In this manner absorption coefficients in the range of 10^{-3} to 10^{-2} cm^{-1} were found, which decreased slightly with increasing initial fuel volume. We suggest that this volume dependence reflects the effect of initial volume on the duration of combustion which could influence carbon partic desnity in the flame. By comparing the radiation measurements of Hardee et al. (1978) for much larger initial fuel volumes of methane with our g gas model it was deduced that the absorption coefficient does not contir to decrease so rapidly with increasing initial fuel volume as we have observed in our laboratory experiments.

For the period after combustion, when the fireball was coolir by adiabatic mixing with the surrounding air, the uniform temperature inferred from the grey gas model was compared with the thermodynamic tem erature calculated from conserving energy inthe product gases. The unif temperature was generally greater than that calculated by the thermodyna model, but the logarithmic rates of decay of the temperatures were nearl the same.

The observations of fireball growth, when compared with the fluid mechanical equations of motion, lead to the conclusion that, durir most of the period of combustion, the average temperature in the firebal is declining. This is in agreement with the temperature histories infer from the grey gas model.

C_p specific heat of air

D fireball diameter

f integral of the dimensionless heat transfer rate

g acceleration of gravity

h_f enthalpy of combustion (lower heating value)

K grey gas absorption coefficient

q_d radiant heat transfer rate per unit area

r distance from fireball center to detector

T_a air temperature

T_f uniform temperature of the fireball

T_p product gas temperature

T_t thermodynamic temperature

t time since ignition

V_f initial fuel volume

z fireball elevation above initial position

Greek Symbols

γ $d(\ell n\ z)/d(\ell n\ t)$

δ dimensionless fireball diameter

η dimensionless time since ignition

ν dimensionless total radiant heat emission rate

$\bar{\nu}$ normalized dimensionless heat transfer rate

ρ_a air density

ρ_f fuel density

ρ_p product gas density

σ Stefan-Boltzmann constant

rocket abort fire model. J. Spacecraft 8, 1216.

rown, L.E., Wesson, H.R., Welker, J.R. (1974). Predict LNG fire radiat
Hydrocarbon Processing 53, 141.

uettner, K. (1951). Effects of extreme heat and cold on human skin, II.
Surface temperature, pain and heat conductivity in experiments with radiant heat. J. Applied Physiology 3, 703.

ay, J.A., and Lewis, D.H. (1976). Unsteady burning of unconfined fuel va
clouds. Sixteenth Symposium (International) on Combustion, The Combu
Institute, Pittsburgh, 1397.

elske, J.D., and Tien, C.C. (1973). Calculation of the emissivity of lu
flames. Comb. Sci. and Tech. 1, 25.

ayle, J.B., and Bransford, J.W. (1965). Size and duration of fireballs
from propellant explosions. TM X-53314, National Aeronautics and Spac
Administration, Huntsville.

ardee, H.C., and Lee, D.O. (1971). A simple heat conduction model for
burns resulting from an incident flux of short duration SC-DC-714047, Sandia Laboratories, Albuquerque.

ardee, H.C., Lee, D.O., and Benedick, W.B. (1978). Thermal hazard from
fireballs. Comb. Sci. and Tech. 17, 189.

ottel, H.C., and Sarofim, A.F. (1967). Radiative transfer, VII. Geome
problems of gas-radiative exchange. McGraw Hill, 256.

ewis, D.H. (1977). The combustion of unconfined vapor clouds burning i
fireball configuration. Ph.D. Thesis, Massachusetts Institute of Tec
nology.

arkstein, G.H. (1976a). Radiative energy transfer from turbulent diffu
flames. Combustion and Flame 27, 51.

arkstein, G.H. (1976b). Scaling of radiative characteristics of turbul
diffusion flames. Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1407.

orton, B., Taylor, G., and Turner, J. (1956). Turbulent gravitational
convection from maintained and instantaneous sources. Proc. Royal So
(London) 234, A., 1.

tional Transportation Safety Board (1972). Derailment of Toledo, Peor and Western Railroad Company's train No. 20 with resultant fire and tank car ruptures. Railroad Accident Report No. NTSB-RAR-72-2. Washington, D.C.

omas, P.H. (1963). The size of flames from natural fires. Ninth Symp (International) on Combustion, The Combustion Institute, Pittsburgh,

en, W.W., and Tien, C.L. (1976). A simple calculation scheme for the luminous flame emissivity. Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1481.

REPORT E

Modeling Detonation and Deflagration Properties of Liquefied Energy Fuels

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TABLE OF CONTENTS

FIGURES

TABLE

SUMMARY

In this report some of the computational models used in the analysis of the detonation and deflagration properties of liquef energy fuels are described. These models include shock wave hy dynamics descriptions and detailed chemical kinetic reaction mechanisms for the specific fuels to be studied. Chemical indu times are calculated using the detailed kinetic models for fuel mixtures typical of LNG. These times are then compared with characteristic shock decay times computed from high explosive c detonations to arrive at a quantitative measure of fuel detonab The effects of minor species in the initial fuel sample, of imp such as water vapor, of fuel-air equivalence ratio, and turbule mixing on induction times and detonability are also investigate

Introduction

In the event of a large scale spill of LNG or other liquefied fuel, the liquid fuel will vaporize and mix with air, as discussed other reports. As the fuel mixes with air, some portion of the fue mixture will become flammable and/or detonable, depending on a vari of factors which are functions of the spill, spill site, the fuel i and many other parameters. In the present work, factors influencin possibility of detonation or deflagration of the fuel-air mixtures being examined by means of computer modeling techniques. This mode program combines the most current information available from experi programs dealing with methane, LNG vaporization and dispersion, dif boiloff, confined and unconfined detonation, shock tube ignition, f structure, and other sources, together with sophisticated fluid mec and chemical kinetics modeling techniques.

The type of modeling approach described here is intended to be coordination with experimental programs, with all portions of the s supporting the others. These models must be validated by means of comparison with experimental data, after which the models can be us assist in the analysis of those experiments and to extrapolate to c which are difficult or expensive to achieve experimentally. Model must occasionally again be verified by means of further experiments primary goal of modeling complex systems such as gaseous detonation flames is to provide additional diagnostic tools to aid in the inte of given experiments and to substantially reduce the cost and time

of a large research program. In addition, model predictions c
indicate potentially fruitful areas for further experimental r
or point out potential dangers.

Models already available at LLL have been used to study s
the physical systems which are important in the analysis of po
hazards arising from LNG spills. These models describe the ev
shock waves generated by charges of high explosives through ai
the chemical kinetic evolution of the chemical species which c
most of LNG. By means of a type of characteristic time analys
sub-models are combined to provide a great deal of detailed in
relevant to the detonability of LNG in air. Other models deve
LLL provide a means of studying flame structure in LNG-air mix
that effects of stoichiometry, composition, trace impurities,
factors on LNG flammability may be evaluated.

Gaseous Detonations

Perhaps the most dangerous hazard which can result from an LEF spill would be the possibility of an atmospheric unconfined gaseous detonation. Detonations can be produced either by transition from deflagration wave or by direct initiation from a blast wave. In ei case there are quite restrictive conditions which must be satisfied the detonation is to continue propagating. The shock wave associat with the detonation compresses and heats a mixture of unreacted gas very rapidly. In the absence of chemical reactions this shock wave will gradually weaken, decaying into a simple compressional sound w It is possible to define a characteristic shock wave decay time, in absence of reaction, as the time required for the shock pressure to from one value to some other value. If the shocked gas is reactive once the shock wave has compressed and heated the gas, chemical rea will begin to take place. At post-shock conditions typical of atmo detonations, these fuel-air mixtures undergo an ignition delay or i period during which chemical reactions take place but little heat is generated. At the end of the ignition delay period, rapid energy r again heats the mixture and raises its pressure further. The heat pressure increase from this reaction are needed to counteract the g decay of the shock wave. Therefore, a useful measure of the stabil a detonation wave can be derived by comparing the characteristic sh wave decay time with the chemical induction time. If the chemical scale is longer than the shock decay time, the detonation will weak

decaying into a sound wave preceding a conventional deflagration the other hand, if the chemical time scale is shorter than or co to the shock wave time scale, the detonation will be stable and to propagate.

The problem of initiation of detonations is an exceedingly one, and a great deal of research is currently in progress with to describing the process. It is not possible at present to acc model the process of transition from deflagration to detonation correlations of experimental data are available (e.g. Lee(1)) wh suggest strongly that transition would be very difficult to achi methane in air under unconfined conditions. However, experimen been performed at the length scales where this phenomenon might so the transition mechanism should not be totally neglected.

The current program to date has concentrated on the proble detonation stability and direct initiation of a detonation by m blast wave generated by a high explosive charge. The relativel analyses reviewed by Lee (1) show that the minimum high explos required to initiate detonation is strongly dependent on geomet factors and for spherical configurations this blast energy woul on the cube of the chemical induction time. One of the product chemical kinetic research at LLL has been a very detailed and w validated kinetics model for methane, ethane and air mixtures. makes it possible to calculate chemical induction times with a

enerality not previously possible. The detonation stability and t initiation processes have been split conceptually into a fluid nical model dealing with the shock wave, and a chemical kinetic dealing with the induction times. We will describe these two odels first and then show how they have been combined to analyze detonation phenomena.

hemical Ignition Delay

A great deal of work has been done in recent years on the ignition f methane in shock tubes, and some studies of the shock tube ignition f ethane and higher alkanes have also appeared. In experiments of his type, a mixture of fuel, oxygen, and diluent (nitrogen and argon) s prepared in the test section of a shock tube. A shock wave is then ropagated through the sample gas, rapidly raising its density, tempera- ure, and pressure to relatively high values. These post-shock conditic n laboratory experiments are similar to those which might be produced n detonation shock fronts. Under these post-shock conditions the fuel irst breaks apart into smaller fragment chemical species. This initia r decomposition phase is followed by a very rapid oxidation phase durin hich these fragments react to form final products, with water and carbo lioxide being the most significant. The progress of this two-phase reac s monitored in several ways, including optical diagnostic techniques ar ressure measurements. For all fuels and conditions of interest to thi eport, the duration of the initiation phase is much longer than the xidation phase. In a typical case, the combined reaction time was 250 ith the final oxidation phase taking less than 1 μsec. The dominance he initiation period is an important feature of the chemical evolution hese systems and we will return to it later. The end of the combined eaction period is characterized by a sharp increase in temperature and ressure as the chemical energy of the fuel is released. This pressure increase during the final fuel oxidation phase reinforces the shock wav a detonation which is propagating under relatively stable conditions.

ta. This is done by constructing chemical kinetic reaction mechanism
ich include all of the relevant elementary chemical reactions which
ke part in the fuel consumption. Temperature dependent rate express
r each reaction are taken from literature sources. A typical reacti
chanism, used by Westbrook (2) in a study related to the present rep
given in Table 1. Conservation equations for each chemical speci
e integrated numerically, using the reaction mechanism and rate
pressions, to determine the time evolution of the system. Within th
amework, the model can compute the evolution of any set of initial
nditions, including those due to an incident shock wave. The princi
tput of this process is the chemical induction time, defined as the
terval between the shock arrival and the rapid pressure rise associa
th the final fuel oxidation phase of the reaction.

The first applications of this technique were to mixtures of
$_4$-O_2-Ar and to C_2H_6-O_2-Ar and reported by Westbrook (2). The detail
netic treatment was shown to be very important in reproducing experi
esults for both fuels. The complexity of the chemical evolution of t
ystems reinforced our impression that no simple model could adequatel
ecribe these experiments. Although global or overall correlation fun
ave been used frequently to describe the induction delay times for sh
ube experiments, these expressions are valid over only a relatively s
ange of post-shock conditions. In addition, global induction time co
rovide no way at all of assessing the influence of the presence of im
uch as water vapor, of mixtures of different fuels, or of other effec
escribed which are important in the analysis of practical fuel reacti

3	$CH_4 + OH \rightarrow CH_3 + H_2O$	3.5	3.08	2.0	Zellner and Steine
4	$CH_4 + O \rightarrow CH_3 + OH$	13.2	0	9.2	Herron (1969)
5	$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$	13.3	0	18.0	Skinner et al. (19
6	$CH_3\ HO_2 \rightarrow CH_3O + OH$	13.2	0	0.0	Colket (1975)
7	$CH_3 + OH \rightarrow CH_2O + H_2$	12.6	0	0.0	Fenimore (1969)
8	$CH_3 + O \rightarrow CH_2O + H$	14.1	0	2.0	Peeters and Mahn
9	$CH_3 + O_2 \rightarrow CH_3O + O$	13.4	0	29.0	Brabbs and Broka
10	$CH_2O + CH_3 \rightarrow CH_4 + HCO$	10.0	0.5	6.0	Tunder et al.
11	$CH_3 + HCO \rightarrow CH_4 + CO$	11.5	0.5	0.0	Tunder et al.
12	$CH_3 + HO_2 \rightarrow CH_4 + O_2$	12.0	0	0.4	Skinner et al. (19
13	$CH_3O + M' \rightarrow CH_2O + H + M'$	13.7	0	21.0	Brabbs and Broka
14	$CH_3O + O_2 \rightarrow CH_2O + HO_2$	12.0	0	6.0	Engleman (1976)
15	$CH_2O + M' \rightarrow HCO + H + M'$	16.7	0	72.0	Schecker and Jos
16	$CH_2O + OH \rightarrow HCO + H_2O$	14.7	0	6.3	Bowman (1975)
17	$CH_2O + H \rightarrow HCO + H_2$	12.6	0	3.8	Westenberg and d
18	$CH_2O + O \rightarrow HCO + OH$	13.7	0	4.6	Bowman (1975)
19	$CH_2O + HO_2 \rightarrow HCO + H_2O_2$	12.0	0	8.0	Lloyd (1974)
20	$HCO + OH \rightarrow CO + H_2O$	14.0	0	0.0	Bowman (1970)
21	$HCO + M' \rightarrow H + CO + M'$	14.2	0	19.0	Westbrook et al.
22	$HCO + H \rightarrow CO + H_2$	14.3	0	0.0	Niki et al. (1969)
23	$HCO + O \rightarrow CO + OH$	14.0	0	0.0	Westenberg and c
24	$HCO + HO_2 \rightarrow CH_2O + O_2$	14.0	0	3.0	Baldwin and Wall
25	$HCO + O_2 \rightarrow CO + HO_2$	12.5	0	7.0	Westbrook et al.
26	$CO + OH \rightarrow CO_2 + H$	7.1	1.3	-0.8	Baulch and Dryso
27	$CO + HO_2 \rightarrow CO_2 + OH$	14.0	0	23.0	Baldwin et al. (1

$H + O_2$	$\rightarrow O + OH$	14.3	0	16.8	Baulch et al. (1973a)
$H_2 + O$	$\rightarrow H + OH$	10.3	1	8.9	Baulch et al. (1973b)
$H_2O + O$	$\rightarrow OH + OH$	13.5	0	18.4	Baulch et al. (1973b)
$H_2O + H$	$\rightarrow H_2 + OH$	14.0	0	20.3	Baulch et al. (1973b)
$H_2O_2 + OH$	$\rightarrow H_2O + HO_2$	13.0	0	1.8	Baulch et al. (1973b)
$H_2O + M$	$\rightarrow H + OH + M$	16.3	0	105.1	Baulch et al. (1973b)
$H + O_2 + M$	$\rightarrow HO_2 + M$	15.2	0	-1.0	Baulch et al. (1973b)
$HO_2 + O$	$\rightarrow OH + O_2$	13.7	0	1.0	Lloyd (1974)
$HO_2 + H$	$\rightarrow OH + OH$	14.4	0	1.9	Baulch et al. (1973b)
$HO_2 + H$	$\rightarrow H_2 + O_2$	13.4	0	0.7	Baulch et al. (1973b)
$HO_2 + OH$	$\rightarrow H_2O + O_2$	13.7	0	1.0	Lloyd (1974)
$H_2O_2 + O_2$	$\rightarrow HO_2 + HO_2$	13.6	0	42.6	Lloyd (1974)
$H_2O_2 + M$	$\rightarrow OH + OH + M$	17.1	0	45.5	Baulch et al. (1973b)
$H_2O_2 + H$	$\rightarrow HO_2 + H_2$	12.2	0	3.8	Baulch et al. (1973b)
$O + H + M$	$\rightarrow OH + M$	16.0	0	0.0	Moretti (1965)
$O_2 + M$	$\rightarrow O + O + M$	15.7	0	115.0	Jenkins et al. (1967)
$H_2 + M$	$\rightarrow H + H + M$	14.3	0	96.0	Baulch et al. (1973b)
C_2H_6	$\rightarrow CH_3 + CH_3$	19.4	–1	88.3	Pacey (1973)
$C_2H_6 + CH_3$	$\rightarrow C_2H_5 + CH_4$	-0.3	4	8.3	Clark and Dove (1973)
$C_2H_6 + H$	$\rightarrow C_2H_5 + H_2$	2.7	3.5	5.2	Clark and Dove (1973)
$C_2H_6 + OH$	$\rightarrow C_2H_5 + H_2O$	13.8	0	2.4	Greiner (1970)
$C_2H_6 + O$	$\rightarrow C_2H_5 + OH$	13.4	0	6.4	Herron and Huie (1973
C_2H_5	$\rightarrow C_2H_4 + H$	13.6	0	38.0	Lin and Back (1966)
$C_2H_5 + O_2$	$\rightarrow C_2H_4 + HO_2$	12.0	0	5.0	Cooke and Williams (19
$C_2H_5 + C_2H_3$	$\rightarrow C_2H_4 + C_2H_4$	17.5	0	35.6	Benson and Haugen (19

Methane-ethane oxidation mechanism. Reaction rates in cm^3-mole-sec-kcal units, $k = AT^n \exp(-E_a/RT)$ cont'd.

	Reaction	Rate			Refe
		log A	n	E	
55	$C_2H_4 + O \rightarrow CH_3 + HCO$	13.0	0	1.1	Davis et al. (1972
56	$C_2H_4 + M \rightarrow C_2H_3 + H + M$	14.0	0	98.2	Just et al. (1977)
57	$C_2H_4 + H \rightarrow C_2H_3 + H_2$	13.8	0	6.0	Benson and Haug
58	$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$	14.0	0	3.5	Baldwin et al. (1
59	$C_2H_4 + O \rightarrow CH_2O + CH_2$	13.4	0	5.0	Peeters and Mahr
60	$C_2H_3 + M \rightarrow C_2H_2\ H + M$	16.5	0	40.5	Benson and Haug
61	$C_2H_2 + M \rightarrow C_2H + H + M$	14.0	0	114.0	Jachimowski (19
62	$C_2H_2 + O_2 \rightarrow HCO + HCO$	12.6	0	28.0	Gardiner and Wa
63	$C_2H_2 + H \rightarrow C_2H + H_2$	14.3	0	19.0	Browne et al. (1
64	$C_2H_2 + OH \rightarrow C_2H + H_2O$	12.8	0	7.0	Vandooren and (1977)
65	$C_2H_2 + O \rightarrow C_2H + OH$	15.5	-0.6	17.0	Brown et al. (196
66	$C_2H_2 + O \rightarrow CH_2 + CO$	13.8	0	4.0	Vandooren and (1977)
67	$C_2H + O_2 \rightarrow HCO + CO$	13.0	0	7.0	Browne et al. (1
68	$C_2H + O \rightarrow CO + CH$	13.7	0	0.0	Browne et al. (1
69	$CH_2 + O_2 \rightarrow HCO + OH$	14.0	0	3.7	Benson and Hau
70	$CH_2 + O \rightarrow CH + OH$	11.3	0.68	25.0	Mayer et al. (196
71	$CH_2 + H \rightarrow CH + H_2$	11.4	0.67	25.7	Mayer et al. (196
72	$CH_2 + OH \rightarrow CH + H_2O$	11.4	0.67	25.7	Peeters and Vinc
73	$CH + O_2 \rightarrow CO + OH$	11.1	0.67	25.7	Peeters and Vinc
74	$CH + O_2 \rightarrow HCO + O$	13.0	0	0.0	Jachimowski (19
75	$CH_3OH + M \rightarrow CH_3 + OH + M$	18.3	0	80.0	Westbrook and

deal of chemical kinetic information is available from these studies of which proved to be very useful in the next validation study of C_2 mixtures. After some development, the mechanism was also able to re experimental data for ethane, as shown also in Figure 1. This com model is the first such mechanism which has been able to simultaneou describe the shock tube evolution of methane and of ethane.

With the mechanism validated at both ends of this compositional spectrum, the model was then used to investigate the evolution of m of methane and ethane, combined first with stoichiometric amounts of Particular attention was directed towards the compositional range wh closest to that encountered in normally-occurring LNG, with approxim 90% CH_4 and 10% C_2H_6. While the kinetic mechanism is not yet able with propane or higher alkane species, there is both experimental an theoretical evidence to suggest that as far as kinetic sensitization induction delay are concerned, propane and ethane behave quite simil

This study of the induction period of methane-ethane mixtures demonstrated several very significant points. First, the addition small amounts of ethane (5-10%) to methane very sharply reduced the time of the composite fuel relative to that of pure methane. This is illustrated in Figure 2, in which the induction time at severa

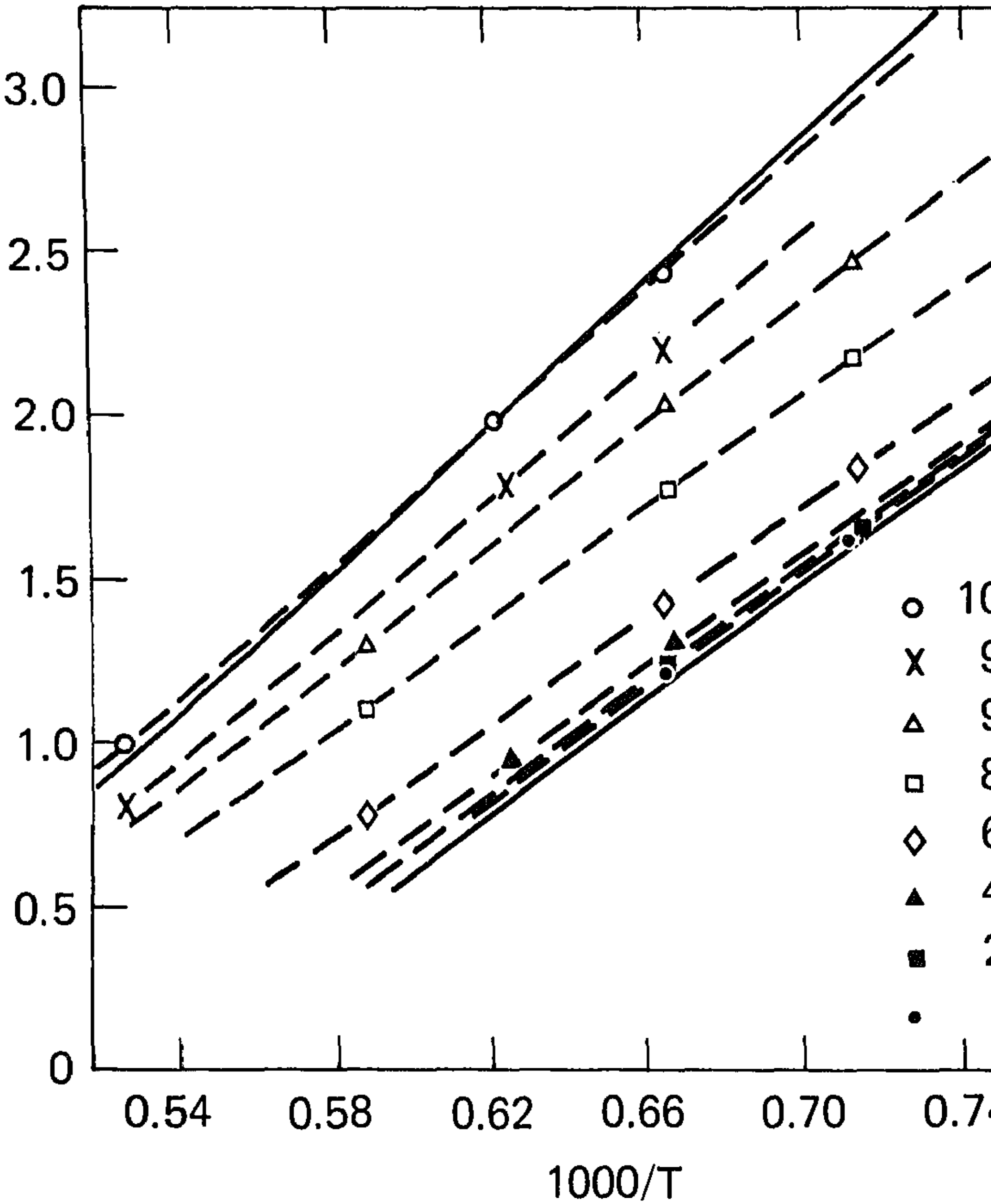

FIGURE 1. Logarithm of the Chemical Induction Time (in μs) at Different Temperatures. (Dashed lines represent computed cases, with the key giving the CH_4-C_2H_6 percentages respectively. Upper solid line shows experimental data for CH_4, lower solid line for C_2H_6.)

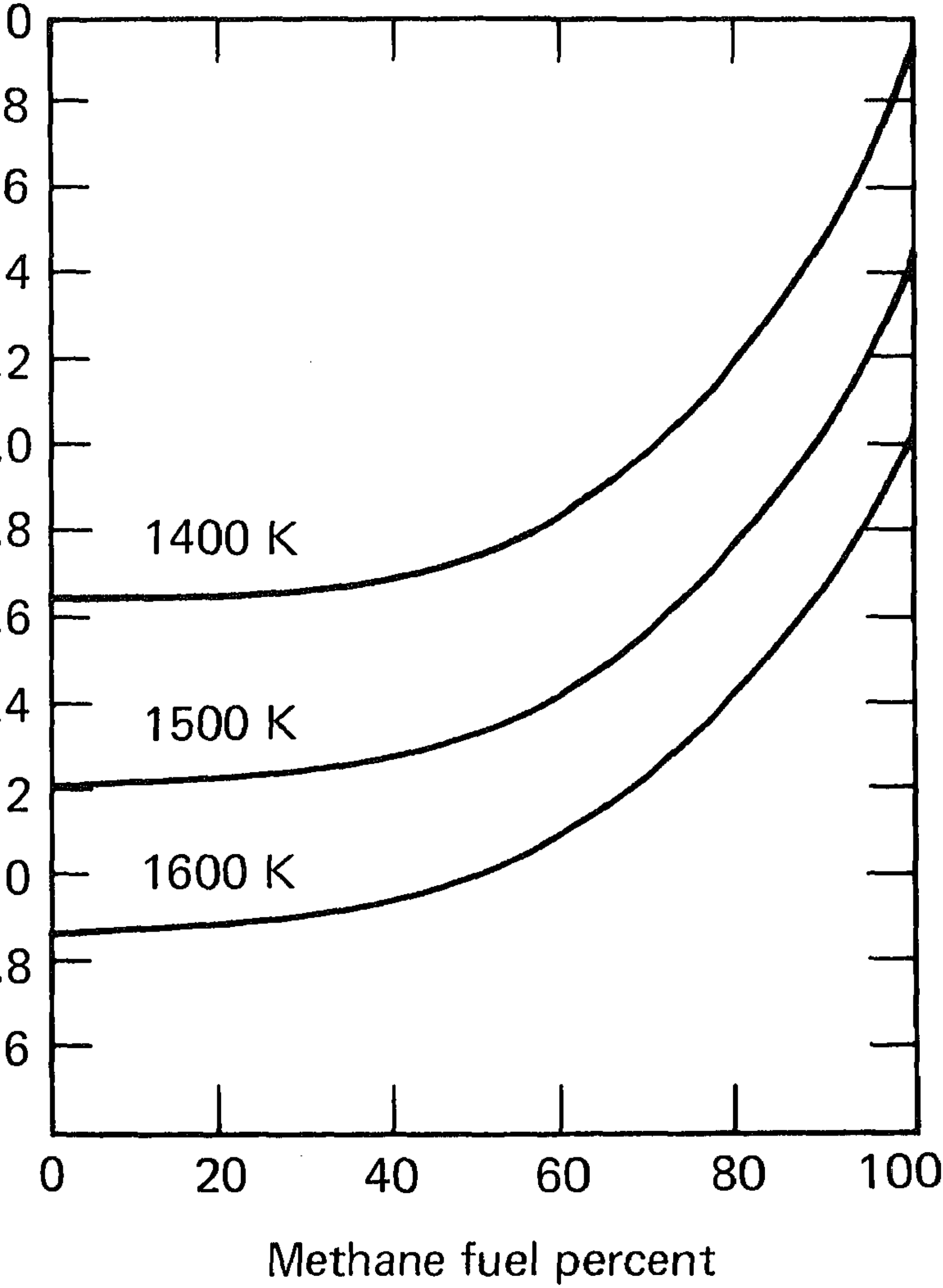

FIGURE 2. Logarithm of Chemical Induction Time (in μs) at Selected Post-Shock Temperatures, Showing the

shock temperatures is plotted as a function of fuel composition. For example, when ethane is 5% of the fuel, the induction time is roughly half that for pure methane. This reduction in induction time by a factor of two would correspond to a reduction in the critical energy for direct initiation of a detonation by a factor of eight according to the discussion presented earlier. The magnitude of this effect is very large and illustrates dramatically the need for detailed chemical kinetic analysis of these systems. In an important sense, the chemica behavior of LNG, at least as far as its detonability is concerned, appears to be dominated by the minor constituents such as ethane and propane.

This work was able to determine the exact chemical mechanism for this fuel sensitization process. Methane itself is difficult to deton due primarily to its very long chemical induction time. The CH_4 molec is unusually stable, with the hydrogen atoms bound very tightly to the carbon atom. In addition, even when a hydrogen atom is abstracted, th resulting methyl radicals (CH_3) are even more difficult to consume. R than react directly, methyl radicals combine together to form ethane ($CH_3+CH_3 \rightarrow C_2H_6$). Much of methane consumption thus proceeds through eth The hydrogen atoms in the ethane molecule are not as tightly bound as methane, and the consumption of ethane is much more rapid than methane More hydrogen atoms are available with ethane, and these hydrogen atom initiate the chain branching reactions which rapidly consume the avail fuel. The kinetic process by which small amounts of ethane can domina the consumption of methane and dramatically reduce the induction times

as seen in Figure 1, not only explains all of the experimental data but also demonstrates conclusively the inadequacy of so-called thermal sensitization mechanisms. In the thermal theory, the more volatile fuel component, ethane or propane, reacts first, releasing a consider amount of heat. That heat raises the temperature of the remaining methane which then would react faster than at its initial temperature. This thermal sensitization mechanism is convenient, but the fuel consumption simply does not occur in that manner. The consumption of two fuels occurs simultaneously, and it is through the free radical c branching reactions that the coupling occurs, not through a sequentia release of heat.

The work done as part of the LNG safety studies at LLL has been to describe the experimentally observed rapid kinetic sensitization o methane by small amounts of ethane and other volatile fuels, and to identify the mechanism by which this occurs. An extremely important result of this mechanism identification and validation is that we now have a theoretical tool which can be applied to other initial conditi with some assurance that the model prediction will be reliable. The evolution of the chemical model from an interpretive tool to a predic one means that the model can be used to try to develop strategies for increasing the safety of the stored fuel, by the use of chemical addi or other means. It can also be used to assess the importance of othe factors which have not been observed experimentally but which might c in spill scenarios. This type of projective use of the model has bee applied for several cases which we will now describe.

Additional Factors Influencing Induction Times

The above studies were carried out for mixtures of methane and ethane, but always with exactly the correct amount of oxygen available to completely consume the fuel. In a typical environment, the vaporize fuel would be imperfectly mixed with air, and the fuel-air equivalence ratio would vary over wide ranges. A series of calculations was carrie out to determine whether or not the observed sensitization due to the presence of small percentages of ethane would occur at other equivalenc ratios. Some of these results are shown in Figure 3, indicating the effects of changes in equivalence ratio on fuel-air mixtures at two different temperatures and two different compositions. The vertical displacement of the pair of dashed lines (1500 K) shows that the sensitization does occur over the entire range of equivalence ratios studied, and the fact that the dashed lines are nearly parallel indica that the sensitization mechanism is effectively independent of equival ratio. The calculated dependence of induction time on equivalence rat is simply due to the fact that it takes more time to consume additiona fuel. The straight lines on Figure 3 suggest that a simple exponent expression could be used to relate induction time to local equivalence ratio in an environment in which the equivalence ratio varied with pos or time. In relating the equivalence ratio to detonability it is impo to recall that in addition to the induction time, the heat release per of gas also has a large effect on the amount of explosive necessary to initiate a detonation. As fuel-air mixtures become more fuel-rich,

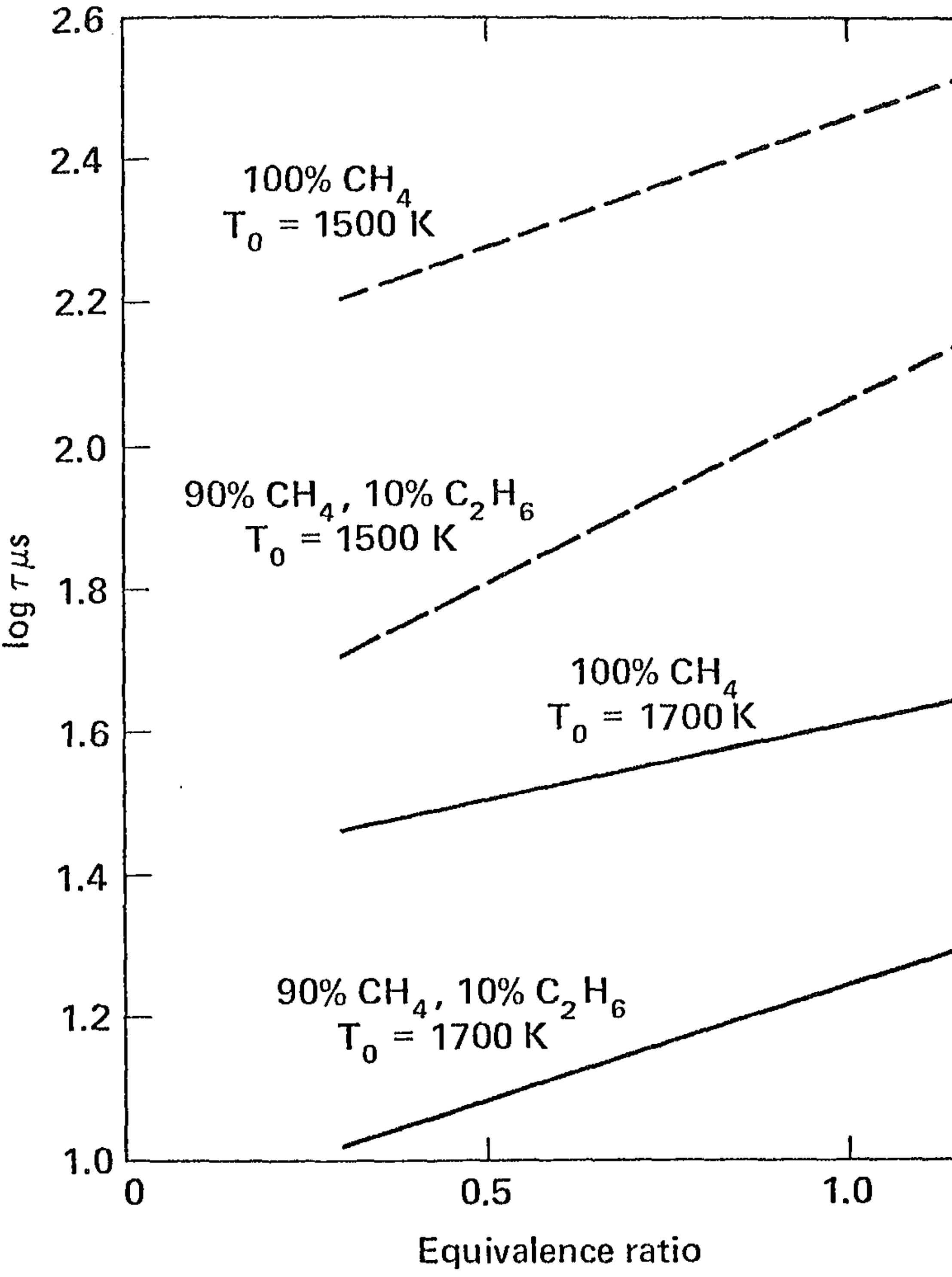

FIGURE 3. Logarithm of Chemical Induction Time (in μs), Showi[ng]
Effect of Fuel-Air Equivalence Ratio, for Selected
Fuel Mixtures and Initial Post-Shock Temperatures.

increasing induction time. As mixtures become more fuel-lean, the temperature decreases with the reduced heat release, so the detonabilit again decreases.

Another factor which might be related to LNG safety studies is the amount of water vapor which would mix with the fuel and air in the event of a spill. In fuel emulsions and other situations where water mixed with hydrocarbon fuels, there is ample evidence to suggest some degree of kinetic coupling between water vapor and the fuel, probably due to the availability of H and OH radicals from the water. There ca be considerable differences in water content in the air between coasta LNG facilities and detonability test sites in the high desert, so the importance of water vapor (if any) needs to be determined. In a serie of computations with the kinetic mechanism above, the effects of the addition of water vapor were examined. The fuel used in the shock tub simulations was composed of 90% CH_4 and 10% C_2H_6, again consistent wit the approximate composition of typical LNG. The results indicated tha at the post-shock pressures and temperatures most likely to be relevan to detonations in the open atmosphere, the presence of water vapor had negligible effect on computed chemical induction times. The temperatu behind the initial shock is too low to cause any significant degree of water molecule dissociation, so the water vapor acts as an inert speci during nearly all of the induction period. This result means that wat vapor has no appreciable effect on the detonability of LNG. Water vap may still have a substantial effect on the flammability and other

properties involved in deflagrations, and work is currently proceedi
in modeling flame properties of LNG with and without water vapor.

The stability of detonation can be enhanced by increasing the turbulent mixing of post-shock gases with combustion products. This is a modified form of kinetic sensitization whereby equilibrium combustion products, containing relatively large concentrations of free radical species, mix with and accelerate the reaction of the fuel, reducing its chemical induction time. Preliminary results in comput already completed indicate that this type of turbulent mixing can ha a significant effect, rapidly reducing the chemical induction time. example, at a 5% mixing level, where 95% of the mixture is unreactec fuel-air and 5% is composed of oxidation products, the induction tin reduced by nearly a factor of two relative to the unmixed case. Adc analyses of these effects are continuing.

An important goal of the purely kinetic modeling program at LLL is the derivation of simplified kinetic expressions for the induction peric and flame propagation rates for relevant fuels. As discussed earlier, i s our feeling that the only systematic and reliable way to produce thes simpler models is through a thorough understanding first of the detailec kinetic mechanisms. Models derived in this way should have wider ranges of validity in terms of physical and chemical effects which can be prope described. Effects such as fuel mixtures, stoichiometry, turbulent mix and others can be handled only if they are first understood in detail. Simplified fits to detailed results described earlier should be valuable as sub-models to be included in multidimensional detonation and deflagra codes being developed in this program at LLL and elsewhere. The use of inappropriate approximations, used because better models are unavailab can thereby be avoided, enhancing the overall reliability of computed predictions. An example of the misuse of simplified rate expressions i the application of global rate expressions derived for post-induction methane oxidation, such as that given by Dryer and Glassman (3), to met oxidation in shock waves. Since fuel-air mixture in detonation shock w is completely un-inducted, the Dryer and Glassman expression is inappro and in fact irrelevant in such environments. What is needed instead is rate expression which describes the induction portion of the fuel consu Similarly, the exponential dependence of induction time on fuel-air equivalence ratio suggests that a simple expression would be applicable account for this effect. Other approximate correlations should be deri from a detailed model before being used in larger fluid mechanics codes

Relating Shock Decay Times to Induction Times

As we described earlier, the progress of a stable detonation depe upon a competition between characteristic time scales. In the absence of chemical reactions the shock wave will decay with one characteristi time scale. If the shocked reactants can release energy quickly enoug to reinforce the shock, then the detonation may continue to propagate. Although we have not assembled a completely coupled numerical model fo reactive shock propagation, we have attempted to combine the results o our models for the shock propagation with our models for chemical induction times to yield a quantitative analytical tool for the analys of a class of detonations. In particular, we have tried to identify t critical conditions for direct initiation of detonations in gases whic are similar to LNG.

A considerable amount of experimental information is available on the detonability of fuels which are either pure methane or primarily methane, in oxygen and in air. These experiments have been carried ou under nearly unconfined, atmospheric conditions and with carefully defined amounts of fuel and oxidizer. In one series of experiments, Bull and co-workers (4) used stoichiometric mixtures of methane and oxygen, diluted with varying amounts of nitrogen. In each case they determined the minimum amount of tetryl high explosive required to initiate a steady detonation in an unconfined spherical configuration One goal of their study was to use results at low nitrogen concentrati where the experiments were simpler to perform, to extrapolate to condi with large amounts of nitrogen (as in normal air) where the experimen

could not be carried out. In the second series of experiments rep
by Bull et al. (5), critical masses of high explosive were determi
various mixtures of methane and ethane in air. These data display
same rapid sensitization of methane by ethane which we described e
in the purely kinetic modeling portion of this report. Again the
were extrapolated to the limit of 100% CH_4, with both extrapolatio
indicating that approximately 22 kg of tetryl would be required to
detonate a methane-air mixture.

Comparisons were made with these series of experiments in a s
of model calculations. For each mixture selected we used an exist
one-dimensional finite difference hydrodynamic computer code to ca
the time dependent shock wave produced in air by spherical charges
Comp-B high explosives for charge masses ranging from 10 gm to 22
shock decay time was chosen as the time required for the shock to
from 20 to 10 bars, so the result of these calculations was a rela
between change mass and shock decay time. This time was found to
the cube root of the charge mass, as would be expected from simple
ments of spherical shock front decay. At the same time, chemical
times were calculated for each mixture, assuming a range of initia
shock temperatures. By equating the chemical induction time with
shock decay time, a correlation was determined between the critica
of high explosive and the initial post-shock temperature of the re
gas mixture. This process of correlation was carried out for both
of experimental data, and each was then extrapolated to estimate t
minimum high explosive charge for a methane-air mixture. In both

xtrapolation gave an estimate of approximately 50 kg of high explosive th this result being very sensitive to the method of extrapolation. ecause the mass of high explosive necessary to initiate a detonation s so sensitive to the temperature at which the induction time is valuated, there is some uncertainty as to the minimum charge necessary o detonate methane-air. Our most reasonable estimate would be that b) and 150 kg of Comp-B would be required.

It must be emphasized again that while there is considerable theo nterest in the initiation of a detonation in methane-air, there is so eason to question how relevant that situation is to practical LNG saf ince LNG contains appreciable amounts of minor chemical species which een determined, both experimentally and in our modeling studies, to ignificantly modify its chemical behavior, predictions of LNG detona ade on the basis of studies of pure methane can be seriously misleadi s noted earlier, with only 5% of the fuel consisting of ethane, the nduction time is half that of pure methane. This translates into a eduction of a factor of eight in the amount of high explosive needed etonate such a mixture, and with a "typical" LNG composition of 90% C nd 10% ethane, propane and other species the critical mass is even sm n addition, the process of differential boiloff, in which the more vo omponent methane evaporates first, will mean that the composition of NG vapor resulting from a typical spill will be progressively richer hese minor constituents. As discussed in another of these reports, p iminary experimental data suggest that the fuel vapor can contain as

importance of considering the role of the species other than metha

A very interesting possibility, at least as far as reduction detonability is concerned, is in the area of impurity removal. Re of the amounts of trace and minor constituents, increasing the fue percentage of methane, could significantly increase the induction and reduce the detonation hazard of LNG. The other logical approa would be to introduce a chemical component which would reduce the detonability of the fuel-air mixture. The detailed kinetic models indicate that such an additive would be most effective if it could remove free hydrogen atoms which are responsible for the chain bra reactions. Much more work, both experimental and computational, i indicated in this area of kinetic modification of the detonable fu

Deflagrations

The propagation of LNG-air flames is being studied, particul in environments which might occur in typical spills. These condi include fuel-air mixtures in which the local equivalence ratio va in space and time, in which the proportions of different fuel con also vary, and in which the amounts of water vapor initially pres the air is a variable.

A much more difficult theoretical and modeling problem which attention is that of assessing the effects of turbulence on LNG-a flames. Of particular relevance is the process by which turbulen can accelerate a deflagration to much larger velocities than conv observed, or even to the point where transition to detonation can Current models cannot yet predict this transition.

The modeling studies described here represent one step in the proc of a thorough description of potential LNG hazards. At the present tim there are several conclusions which can be drawn from the computational analysis.

The first major point is that it is very important to remember tha typical LNG is not composed only of methane, but that approximately 10% of LNG is made up of ethane, propane, and other species. The induction time calculations described here show that this 10% makes a great deal difference in the induction time and therefore in the detonability of L Studies which have not or do not take this composition into account may not be applicable to the question of the detonability of LNG vapor. Th impurities or minor constituents play a major role in determining the induction time and detonability of LNG.

Another important conclusion is that the purely kinetic model described here has been validated by comparison with experimental data can be reliably applied to other sets of conditions which have not rece experimental attention. This was done to examine the possible effects turbulent mixing, the presence of water vapor, and effects of fuel stoichiometry, in addition to the methane-ethane mixing already describ In addition to providing additional diagnostic capability, these models indicate areas in which further experimental study is needed, and in wh potential dangers might exist.

Finally, the characteristic time analysis described was used to c available experimental data on unconfined detonations. Extrapolations

le to estimate that a high explosive mass of 50-150 kg of Comp-B wou required to detonate a stoichiometric methane-air cloud. However, appears that the problem of methane-air detonation may be of doubtf evance to the subject of LNG detonability, since it was demonstrate at minor species in LNG sharply modify its detonability.

ferences

Lee, J. H., Initiation of Gaseous Detonation Annual Reviews of Physical Chemistry 28, 75 (1977)

Westbrook, C. K., An Analytical Study of the Shock Tube Ignition of Mixtures of Methane and Ethane, Combustion Science and Technolo to be published. Also available as University of California Lawrence Livermore Laboratory Report UCRL-81507, July 1978.

Dryer, F. L., and Glassman, I., High Temperature Oxidation of CO and CH_4, Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1973.

Bull, D. C., Ellsworth, J. E., Hooper, G., and Quinn, C. P., A Study of Spherical Detonations in Mixtures of Methane and Oxygen Diluted with Nitrogen, J. Phys. D. 9, 1991 (1976).

Bull, D. C., Ellsworth, J. E., and Hooper, G., Initiation of Sphe Detonation in Hydrocarbon/Air Mixtures, presented at the Sixth International Colloquium on Gasdynamics of Explosions and Reactiv Systems, Stockholm, Sweden, 1977.

REPORT F

LNG Release Prevention and Control

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U.S. Department of Energy
under Contract EY-76-C-06-1830

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Operated by Battelle Memorial Institute

TABLE OF CONTENTS

FIGURE

TABLES

This status report discusses Pacific Northwest Laboratory's (PNL) in the LNG release prevention and control area. The basic objective o LNG Release Prevention and Control Project is to develop an adequate u standing of LNG release prevention and control systems and the factors may defeat them. Each type of existing LNG facility is considered. T basic work areas are defined: system definition, safety analyses and gathering. The report discusses the technical progress and future pla each of these areas. The preliminary results of a scoping assessment release prevention and control systems of a generic peakshaving plant described. Early results indicate that any more detailed safety analy should concentrate on the LNG storage and vaporization systems.

The LNG industry employs a variety of release prevention and co
mechanisms which contain LNG during transfer and storage and which c
control an LNG release if it occurs.

The objective of the LNG Release Prevention and Control Projec
develop an adequate understanding of LNG release prevention and cont
and the factors which may defeat them. Some more specific objective

- Identifying the important features and possible weak links of r prevention and control systems.
- Identifying data needs and information gaps in the release prev and control area and providing recommendations for obtaining th additional information through data gathering, analytical studi experimental studies.
- Identifying potential areas where release prevention and contro can be cost and safety effectively improved.

Release prevention and control systems can be divided into thre

1) Release Prevention - systems or components which contain LNG du normal process operations and anticipated process upsets.
2) Release Detection - systems or components which detect an LNG r once it occurs.
3) Release Control - systems or components which stop or control a release.

Each of these areas will be considered but the primary initial empha
the project is the release prevention area. Vapor control systems a
control systems and their effectiveness are not considered directly
project at its present stage.

Each type of existing LNG facility is considered in the projec
LNG facilities are grouped into the following work packages:

3) Export terminals, ships and import terminals

hese groups are reflected in the project task descriptions and represent onvenient way of treating the LNG facility interfaces.

A staged approach is used to accomplish the project objectives. A eneric description of each LNG facility is developed. This system descr ion is used to perform a scoping or first level analysis (initially a pr iminary hazards analysis followed by a failure mode and effect analysis) dentify information needs and potential release prevention and control a hich may merit more detailed study. The feasibility and methods of obta he required additional information are investigated and a decision is ma hether to perform a more detailed assessment (possibly a refined failure nd effect analysis or, if the system detail and data warrant it, a fault ree/event tree type analysis). In conjunction with this assessment, ana nd experimental studies are recommended to fill information gaps.

This project was initiated in FY-1978. The status as of the firs
quarter of FY-1979 is that the draft generic system descriptions have
completed for the basic types of LNG facilities. The scoping safety a
was completed for the peakshaving facility and the more detailed analy
been initiated. The scoping safety analyses for the remaining LNG fac
have been initiated.

Three basic interrelated work areas have been defined for the LNG
Prevention and Control Project. These are system definition, safety a
and data gathering. The results of the project to date are discussed
these topics.

SYSTEM DEFINITION

Generic descriptions for the basic types of LNG facilities have b
prepared. These include:

- Peakshaving Plant
- Import Terminal
- Export Terminal
- Marine Vessel
- Satellite Plant
- Truck Tanker

PNL selected representative equipment sizes and process options for th
generic facilities.

The unit operations which make up the LNG peakshaving facility ar
treatment, liquefaction, storage, and vaporization. The gas treatment
utilizes molecular sieve adsorbers to remove water and CO_2. The lique
unit has a capacity of 6.0×10^6 SCFD and utilizes an integrated casca
refrigeration process with a mixed refrigerant of methane, ethylene, p
and nitrogen. After liquefaction, the LNG is stored in an above-grour
double-walled storage tank with a capacity of 348,000 BBL. The inner
genic barrier is an aluminum alloy and the outer tank is constructed o
steel. Submersible LNG pumps send the LNG from the storage tank to su
combustion vaporizers. The gas from the vaporizers then goes to the p

through loading arms to a transfer line and on to the storage tanks
approximate rate of 53,000 gpm. The storage tanks are two 550,000
ground, double-walled metal storage tanks of the standard design fo
Submersible in-tank pumps transfer the LNG to the secondary pumps w
fer the LNG to the vaporizers. The facility has a total of nine va
Five of these are seawater heated with a total capacity of 550 x 10
are used for normal operations. Four are submerged combustion vapo
a total capacity of 450 x 10^6 SCFD and are used as spares. The gas
vaporizers is introduced into the pipeline.

The unit operations which make up the export terminal are gas
liquefaction, storage, and shore to ship transfer. The natural gas
the plant is passed through an monoethanolamine (MEA) scrubber and
utilizing molecular sieves prior to entering the liquefaction secti
liquefaction section is a propane precooled multirefrigerant cycle
methane, ethylene, propane and nitrogen as a mixed refrigerant. Th
faction system is rated at 400 MMCFD. LNG exiting the liquefaction
is pumped into two 550,000 BBL, double-walled, above-ground metal s
of the standard design for LNG. LNG is then transferred from the s
tanks to the vessel at a rate of 50,000 to 60,000 gpm.

The 125,000 m^3 marine transporting vessel has a range of appro
10,500 nautical miles. The cargo system includes five spherical al
tanks. Two unloading pumps each with a capacity of 1040 m^3/hr are
in each tank. The LNG tanker has a double-hulled structure through
vessel to reduce the possibility of damage to the cargo tanks in th
of a collision or grounding.

The unit operations at the satellite facility are truck-traile
storage and vaporization. LNG is unloaded from a truck-trailer at
150 to 350 gpm to a 37,000 BBL, above-ground, double-walled, metal
tank of the standard design for LNG. Submersible LNG pumps then se
to two submerged combustion vaporizers with a rating of 24 MMSCFD.
vaporizers the LNG is then transferred to the pipeline. The LNG tr
is a double walled perlite filled, vacuum insulated vessel with a g
capacity of 11,550 gallons.

rces of information. These include Federal Energy Regulatory Commissio ic files, LNG equipment vendors and the open technical literature. Th el of detail in the generic system description includes process flow ra sel and piping sizes and material of construction, types of valves, con tem operations, startup and shutdown procedures, etc.

As was expected, there were areas for which little or no information ilable. One of the purposes of the scoping safety analyses is to ident important release prevention and control areas so that information nee be filled in an efficient manner.

TY ANALYSES

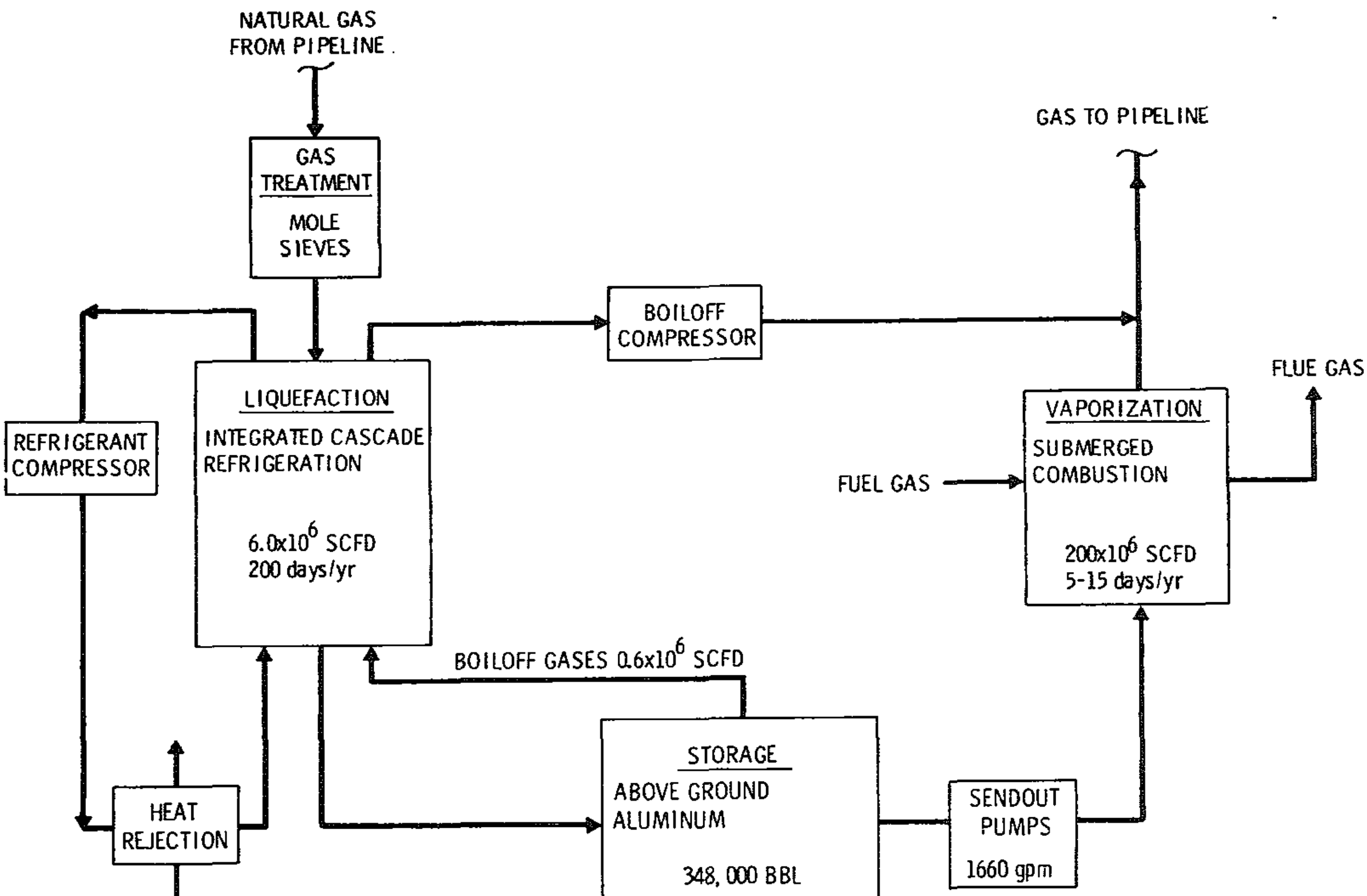
As discussed in the introduction, a staged approach consisting of an tial preliminary hazards analysis followed by a more detailed analysis d to analyze the LNG release prevention and control systems. The early lts of the generic LNG peakshaving facility scoping safety analysis ar cussed in this section.

Figure 1 illustrates the basic unit operations which make up an LNG kshaving facility. They are gas treatment, liquefaction, storage, and orization.

The gas treatment system consists of an inlet separator, a moisture a removal unit (molecular sieves) and a regeneration gas heater, cooler, compressor.

The liquefaction unit is comprised of a cold-box, refrigerant compres coolers and refrigerant storage. The cold-box consists of nine heat hangers, four vessels, and associated piping and instrumentation all su nded by perlite insulation and enclosed in a steel shell.

Refrigeration for the unit is provided by an integrated cascade refri tion cycle which provides progressive gas cooling (i.e., gas condensati successive cooling stages) using a multiple component refrigerant. The densation pressure is the same for all stages (490 psia) and likewise t



NATURAL GAS FROM PIPELINE
GAS TREATMENT
MOLE SIEVES
REFRIGERANT COMPRESSOR
LIQUEFACTION
INTEGRATED CASCADE REFRIGERATION
6.0x10^6 SCFD
200 days/yr
HEAT REJECTION
BOILOFF COMPRESSOR
BOILOFF GASES 0.6x10^6 SCFD
STORAGE
ABOVE GROUND ALUMINUM
348, 000 BBL
SENDOUT PUMPS
1660 gpm
GAS TO PIPELINE
FLUE GAS
FUEL GAS
VAPORIZATION
SUBMERGED COMBUSTION
200x10^6 SCFD
5-15 days/yr

e at each stage. The resulting liquid then is revaporized at a sure (47 psia) hence a lower temperature.

ge for the facility is a standard flat bottom double-walled above- storage tank with a capacity of 348,000 BBL. The inner tank is d of aluminum-magnesium alloy AA5083. Aluminum-magnesium alloys, steel and 300 series stainless steels all possess excellent low e ductility and can be used as construction materials for the . Carbon steel, which has a very poor low temperature ductility, r the outer tank. The diameter of the inner tank is 164 ft and the f the outer tank is 173 ft.

hree LNG sendout pumps are vertical submerged, pot-mounted LNG pump The pumps and the motor drives are hermetically sealed in a vessel ged in LNG. This design is advantageous in that the extended shaft sociated seal is eliminated. The pump and motor surroundings are with LNG and will not support combustion. The pumps are mounted in pot below grade to provide sufficient suction head for operation. has a capacity of 100 MMSCFD or 830 gpm for a total rated sendout f 200 MMSCFD with one pump as a spare. The operating temperature and the discharge pressure is 945 psia.

aporizers for the plant are four submerged combustion units each 0 x 10^6SCFD capacity. The total rated vaporization capacity of the 50 x 10^6SCFD with one vaporizer considered a spare.

ef approximate analysis to determine maximum release rates for the ctions of the generic peakshaving facility was performed. Table 1 mated releases due to postulated pipe breaks in various parts of akshaving plant. A ten-minute time is abritrarily assumed to be o stop the initial release. As seen from Table 1, based on the mptions, the largest potential releases are from the storage tank G pumps. The values given are only useful for comparative purposes.

ing upon this analysis, a preliminary hazards analysis was per- each of the peakshaving facility unit operations. The effect of

TABLE 1. Postulated Releases from Pipe Breaks in a Peakshaving Facilit

Location of Break	Continuous Leak Rate SCFM[a]	Total Release (10 m SCF[a]
Gas treatment system outlet (100% vapor 485 psia)	4.4×10^3	4.4×10^4
Liquefaction outlet[b] (4% vapor 15.8 psia)	4.4×10^3	5.7×10^4
Liquid outlet from tank (0% vapor 15.8 psia)	2.4×10^6	2.4×10^7
LNG pump outlet header[b] (0% vapor 900 psia)	1.4×10^5	1.7×10^6
Vaporizers outlet (100% vapor 870 psia)	1.4×10^5	1.4×10^6

(a) SCFM ≡ standard cubic feet per minute
(b) includes release contribution of liquid holdup in system

initiating events such as equipment failures, operator errors and externa events were qualitatively analyzed. For active type components (e.g. mot electrical components, etc.) it was typically found that two or more sepa failures were required to result in any significant release. For most of passive type components, (e.g. piping, process vessels, etc.) a single failure can result in an initial release but emergency shutdown systems a designed to stop the initial release. One obvious exception is the gross failure of the inner storage tank. The probability of this type of event be minimized with proper design and operating procedures.

The scoping analysis has identified some areas for additional study more detailed analysis. In any additional analysis the following factors be important:

- Interactions between the basic LNG peakshaving operating system hard and release prevention and control hardware
- The human interface
- Common Cause Failures
- Design Adequacy

more detailed analysis of peakshaving release prevention and control. me examples include:

- More detailed engineering drawings
- More detailed description of operating startup and shutdown procedu
- Maintenance and testing procedures

Based upon early results the more detailed analyses will concentrat e LNG storage and vaporizations systems. The scoping analysis is of a minary nature and any initial conclusions must be verified by addition udies. Data gathering efforts are being initiated to fill the identif formation and these additional studies are underway.

As was discussed in the introduction, the initial emphasis of the p minary hazards analysis was the release prevention area. The next ste the analysis is to systematically analyze the release detection and r ntrol systems and their response to postulated LNG releases. A Federa ergy Regulatory Commission Cryogenic Safety Review[1] has identified a mber of operational and safety related considerations for the cryogeni rtions of LNG facilities under its jurisdiction. Table 2 lists some o ese areas. These, along with results from the preliminary hazards ana her areas identified in the literature and by previous LNG operation e ce, will form the basis for postulating a list of initiating events to ed in systematically analyzing the response of the release prevention ntrol equipment.

TA GATHERING

Data sources used in the scoping analysis consisted primarily of th en technical literature, LNG equipment vendors and Federal Energy Regu mmission public files. Some basic areas of interest are details on LN cility descriptions and operating procedures, previous LNG operating perience and LNG equipment failure rates. A broad list of potential d urces is being prepared. Some potential sources include LNG facility erators and designers, LNG equipment vendors, the U.S. Coast Guard, th S. Department of Transportation, the American Gas Association, the

TABLE 2. Example Operational and Safety Related Areas for LNG

storage tank specifications;
storage tank penetrations;
storage tank withdrawal lines/internal valves;
storage tank design;
LNG piping connections;
storage tank internal bottom fill piping/downcomer design;
feed gas composition;
LNG storage tank fluid stratification;
storage tank pressurization level;
storage tank thermocouple monitoring;
variation in gas heating value;
storage tank internal valve setting;
storage tank instrumentation/liquid level detection problems;
storage tank overflow indicator details;
plant attendance/telemetered data;
storage tank vacuum breaking;
storage tank floor insulation material selection criteria;
storage tank purge header design and material selection;
storage tank purge-out-of-service (decommissioning) procedure
retention of natural gas in inert gas-purged insulating materi
storage tank settlement details;
relative elevations: storage tank, impoundment area, dike wal
storage tank impounding area capacity;
storage tank cooldown;
storage tank relief valve discharge orientation/design details
protection
storage tank discretionary vent operating details;
liquefier specifications;
liquefier design;
cold-box details: access, flanged connections, insulation mat
liquefaction process description, flow diagram;
refrigerant storage capacity;
refrigerant system equilibration pressure during plant shutdow
refrigerant disposal system;
facility vent stack/flare stack philosophy;
facility vent collector system;
facility fire protection/hazard control systems;
facility control system;
facility fire protection/hazard control systems specifications
facility combustible gas sensor locations;
facility firewater systems: pumps, lines, tanks;
LNG sendout pump problems: winding failures, flange leaks;
emergency shutdown and operating procedures.

licly available information will be sought and suggested methods for plementing this, if required, will be identified.

A brief survey was made of the utility regulatory agencies of twenty-r states which have LNG facilities. The survey asked what regulatory uirements the state had and whether reporting of LNG spills and other ormal occurrences was required. Nineteen state agencies responded and results are shown in Table 3.

FUTURE PLANS

The planned work for FY-1979 includes: 1) complete the scoping safet lysis for each LNG facility, 2) initiate a data gathering program, refine the system description for each LNG facility, and 4) initiate a e detailed safety analysis of the peakshaving facility.

REFERENCE

Chelton, D. B., A. F. Schmidt, T. R. Stobridge, "Cryogenic Safety Rev Western LNG Terminal Company FPC Docket No. CP75-83-3, NBS - Institut for Basic Standards, January 23, 1976.

State	Regulations for Intrastate Facilities	Reporting Requirements for
Pennsylvania	Pennsylvania Public Utilities Commission has adopted Parts 191, 192 Title 49, CFR (NFPA 59A)**	None
New Jersey	New Jersey has agreement with OPSO to monitor intrastate public utilities for compliance with Parts 191, 192 of Title 49 of Code at Federal Regulations. Therefore state requires LNG facilities to meet NFPA 59A.	Public utilities are requir abnormal occurrences - none
Wisconsin	No regulations on intrastate facilities.	None
Virginia	Each intrastate facility must make detailed presentation to Virginia State Corporation Commission for approval of project. Presentation must cover costs, financing, location, construction, operation and safety. Safety considerations exceed NFPA. No written regulations.	Regular reporting requirem interruptions, and all ope
Illinois	Illinois Commerce Commission has adopted Part 192, Title 49 of Code of Federal Regulations (NFPA59A)	None
Nebraska	No state agency regulates LNG facilities. State Fire Marshall has some general safety regulations which apply to LNG facilities. Cities and municipalities have the regulating responsibility	None
South Carolina	No regulations other than Parts 191 and 192, Title 49 for interstate facilities.	None
Georgia	No regulations other than Parts 191 and 192, Title 49 for interstate facilities.	None
Indiana	No regulations other than Parts 191 and 192, Title 49 for interstate facilities.	None
Iowa	Operations and safety matters related to LNG are under the State Fire Marshall's office in the Department of Public Safety. The Public Safety Department has adopted NFPA 59A into its Iowa Department Rules.	-
Maryland	No regulations on intrastate LNG facilities	None
Arkansas	Arkansas Public Service Commission has adopted NFPA 59A for intrastate facilities	Same as OPSO requirements
Tennessee	Approval of Tennessee Public Service Commission for construction and operation is required. No written regulations for intrastate facilities.	None - Have had one reported facility as part of OPSO re
New York	Intrastate facilities are regulated by NY Public Service Commission under Title 16, NYCRR Part 259-Liquified Natural Gas.	Companies are required to r LNG facilities may be invol injury or damage to propert concern.
Oregon	NFPA 59A enforced by State Fire Marshall and Oregon Public Utilities Commission Oregon State law has adopted Part 192, CFR.	State law requires reportin outages resulting in death hospitalization damage of $ of gas, or a significant ev
California	The State Public Utilities Commission is currently drafting regulations governing construction, operation, and safety of LNG facilities.	-
Washington*	No regulations on intrastate facilities.	None
South Carolina*	No regulations on intrastate facilities.	None
Minnesota*	No regulations on intrastate facilities.	None

* These states answered by telephone, all others were by letter. Five states surveyed did not answer. Questionnaires were sent to all 24 states that have LNG facilities.

** Parts 191, 192, Title 49, CFR (NFPA 59A) refers to the section of The Code of Federal Regulations which applies to Liquefied Natural Gas facilities. NFPA 59A is the standard of the National Fire Protection Association which applies to LNG facilities. This standard is included as a major portion of the Federal Code. The Federal Code is enforced by the Office of Pipeline Safety Operations (OPSO) under the Department of Transportation (Note: OPSO has recently been changed to OPSR, the Office of Pipeline Safety Regulations). The Federal Code applies to all interstate gas companies (those which move gas across state lines) but does not affect intrastate companies.

REPORT G

The Feasibility of Methods and Systems for Reducing LNG Tanker Fire Hazards

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U.S. Department of Energy and the
Office of Commercial Development,
Maritime Administration
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TABLE OF CONTENTS

FIGURES

eased in a major accident, for altering the physical and chemical sta the natural gas, and for using fire suppressants as a means of dimini .ker fire hazards were considered. The evaluation also included syste · protecting the LNG tanker and its crew from the thermal effects of a :ge fire and methods for disposing of the cargo from a damaged and/or sabled tanker.

This study focused on tankers carrying about 125,000 cubic meters o G. Ships of both the membrane and free-standing tank design were cons

A rapid spill of the entire contents of one LNG cargo tank (~25,000 s considered in this report, as the basic accidental event. In risk s .rformed for various projects, this collision accident has been conside representative of the most hazardous occurrence deemed credible.

The principal approaches to reducing LNG tanker hazards that were c idered in this study consisted of modifications to the ship and/or its argo so that the magnitude of the fire would be decreased if a spill sh ccur. Generally, there is little that can be accomplished in the way o ire fighting or inerting the flammable vapor once a large spill has occ ethods that might be applied to ships already built (as for example, by it) are regarded to be of particular importance because many of the shi rill be used in U.S. LNG trade over the next 10 to 20 years may be eithe inder construction or already in service.

1.0 INTRODUCTION

Liquefied natural gas (LNG) tankers are presently servicing U.S. import and export terminals on a regular basis, and the implementation of plans for additional import facilities will significantly enlarge tanker traffic in the future. It has been estimated,[1] for example, that, "in a few years . . . each day, on the average, about 200,000 cubic meters of LNG could be in transit, in U.S. waters, in places lik Boston, Chesapeake Bay, Savannah River, Lake Charles, La., Matagorda Bay, Tex., somewhere in California, and Alaska." This is roughly equiv lent to about one fully loaded tanker transiting U.S. waters every day of the year, plus another tanker every other day.

The current and projected tanker operations present risks to property and life along various U.S. shipping channels. In fact, a major cargo spill might cause an exceptionally large fire which could effect thermal damage and injury over considerable distances beyond th area of the spill itself. However, the harmful risks have been examined in great detail for most LNG import programs, and it is generally concluded that the likelihood of a major accident occurring is remote--so remote, in fact, that a large spill would not be expecte to occur during the projected lifetimes of these projects. In additio the extraordinary measures that are currently being enforced by the U. Coast Guard, along with continuing attention to improvements in shippi operations, are expected to reduce these risks even further.

In spite of the very small chance that a large accident could occ the consequences of such an accident remain quite large. The addition lowering of such risks, then, are potentially achievable by the imple-

(1) Johnson, P., "Overview of OTA's Assessment, entitled "Transportati of Liquefied Natural Gas: Safety Siting and Policy Concerns;" Committee Reprint, Committee on Commerce Science and Transportatio United States Senate, June 1978.

of the accidents. The evaluation of the feasibility of employing suc methods and systems to reduce the consequences of tanker accidents by the amelioration of LNG tanker fire hazards is the subject of this report.

In this study, we considered methods of reducing the rate and/or quantity of LNG that might be released in a major accident, technique for altering the physical and chemical state of the natural gas, and the use of fire suppressants as a means of diminishing tanker fire hazards.

In addition, we considered systems for protecting the LNG tanker its crew from the thermal effects of a large fire and methods for dis of the cargo from a damaged and/or disabled tanker as approaches to preventing the escalation of an accident involving the spill from one or, at the most, two cargo containers.

2.0 PROGRAM OBJECTIVE AND APPROACH

objective of this program was to identify and evaluate new and ncepts for reducing the hazards presented by LNG tanker transits able waters in the United States. The study also included a ary assessment of the technical and economic (construction costs) ity of the concepts that were identified.

ERAL APPROACH

this study, we focused our interest on tankers that transport abou cubic meters (M^3) of LNG, since we expect them to be predominant LNG shipping trade and, in fact, are currently the largest ships in . Ships of both the membrane and free-standing tank design were red.

rapid spill of the entire contents of one LNG cargo tank (~25,000- generally used as the basic accidental event, in this report, sin olume is characteristic of a potential spill expected by the collis rge ship with an LNG tanker. In risk studies performed for variou ts, the collision accident has been considered as representative of st hazardous occurrence deemed credible.

he principal approaches to reducing LNG tanker hazards that were ered in this study consisted of modifications to the ship and/or rgo so that the magnitude of the fire would be decreased should a occur. Generally, there is little that can be accomplished in the fire fighting or inerting the flammable vapor once a large spill ccurred. Methods that might be applied to ships already built (as xample, by retrofit) are regarded to be of particular importance si of the ships that will be used in the U.S. LNG trade over the next years may be either under construction or already in service.

2.2.1 Methods of Reducing Spill Rate and Quantity

2.2.1.1 Hazard Reduction

The penetration of an LNG cargo tank of an existing tanker, such as could happen in a major collision, is apt to result in the release of th entire contents of the tank within a few minutes. In fact, the spill time has been estimated to be so short that the modeling of spill hazard in most prior risk estimates assumes, for reasons of simplicity (and conservatism), that the LNG spills instantaneously.

To establish the gains to be made by slowing down the rate of release and/or limiting the total amount that is released in a single spill, estimates have been made of the resultant decrease in pool fire and vapor cloud hazards. An example of the results of these estimates i presented in Table 2.1. The table shows that by reducing the spill size only 1,000-M^3 rather than 25,000-M^3, and by causing the spill to occur at a constant rate of some 30 minutes or more rather than near instanta-neous, the thermal radiation hazard from a pool fire would be so curtail that significant thermal effects would remain essentially within the vicinity of the spill; i.e., within about 400 feet of the center of the spill. The size of the potential vapor cloud (under adverse meteorologi conditions) would also be diminished; however, it would still present a hazard some 4500 feet from the center of the spill. Greater reductions are theoretically possible, but become more difficult and expensive to achieve.

2.2.1.2 Methods

Presently there are four different ways in which the accidental spi quantity or rate of release of LNG may be reduced. Each is described be

(1) Partitioning of Existing Tank Designs - Cargo tanks may be divided into separate compartments so that when a collision occurs only the LNG in the compartment that is accidentally penetrated wou be released. To partition tanks in this manner, however, requires

TABLE 2.1

THERMAL RADIATION AND VAPOR CLOUD HAZARDS FOR DIFFERENT SPILL SIZES AND SPILL DURATIONS

Spill Size, m^3	Spill Duration, min.	Distance of Harmful Thermal Radiation from Pool Fire, m*	Maximum Travel of Vapor Cloud, Km**	Maximum Half Width of Vapor Cloud, m
5,000	"instantaneous"	2100	20	700
	10	900	10	300
	30	550	3.2	150
0,000	"instantaneous"	1500	14	500
	10	600	7.5	200
	30	350	2.7	100
1,000	"instantaneous"	660	5	200
	10	190	2.8	70
	30	120	1.4	35

distance from center of spill where radiation = 5 kW/m^2

Maximum travel distance of unignited flammable vapor cloud assuming flammable limit is 5% methane in air, atmosphere condition F

to the liquid in the remaining compartments would also have to be accomodated.

A review of the designs of LNG tankers already built or under construction indicates that there are several difficulties associate with this approach. It does not appear feasible to insert bulkheads or partitions in existing membrane systems within a reasonable cost since the membrane linings will not in themselves provide adequate support. The free standing spherical containers will support partitions but because of the increased difficulties in analyzing stresse in such a system there is some possibility that the classification of the tanks would be changed; thus introducing the requirement that a full secondary cryogenic barrier be introduced. This would not appear to be practical.

Only the self supporting rectangular tanks of the Conch design may be receptive to the installation of partitions without introducing other severe problems, but there is a limited number of ships of this configuration. In any event, either a large number of partitions or a complex and expensive design would be required in order to achieve large reductions in spill quantity. Partitionir of tanks may be most cost effective, however, when combined with other approaches such as the addition of filler material that would restrict the outflow of LNG.

(2) Multi-tank Ship Designs - There are two ship designs that utiliz a large number of smaller cargo tanks being proposed for LNG trade. One of these being offered by Verolme uses 3,400-M^3 uninsulated vertical cylinders located in groups within insulated holds in the ship. The major effort by Verolme at present is concentrated on a large vessel design, with a payload of 330,000-M^3. Spillage of LNG by penetrating the ship in a collision would be greatly reduced, but the flooding of the hold in such a case may create venting problems for the undamaged containers.

The other ship design referred to as the OCEAN PHOENIX uses a complex system of partially compartmented multi-lobed vessels for LNG containment at pressures in the 40 to 70 psi range. This design provides the advantage of reduced spill rates in an accident, but bursting of pressurized vessels due to thermal exposure could resu in explosions and possible propagation of the failure to other tanks.

Since both of these ship designs are being proposed as competitiv alternatives to existing ship configurations, their cost may be near that of ships now being built of similar capacity.

(3) Insertion of Open Cell Filler Material - The object of this approach would be to restrict the flow of LNG from the container by requiring it to pass through small restrictions within an open celled filler material that has been placed in the tank. This principle has been applied to small flammable liquid containers using open-cell foams or rolled-up sections of expanded aluminum to form a cell-like structure within the tank. Only a few percent of the container volum is occupied by the filler material. Additional analysis is required however, before the loss of cargo space and the restriction of outfl from an LNG tank may be established.

A variation of this approach utilizing much less filler would be the installation of partitions of material suspended as curtains which would tend to block tank openings created by ship collision penetrations. The rate of outflow would be reduced by the impedence offered by the small passages through which the LNG would have to travel.

This approach appears to warrant further investigation, at leas as a potential hazard reduction technique that might act as a retro fit for the free standing tank designs.

(4) Combine Cellular Filler Material with Compartmentalization - This approach offers the opportinuty of reducing both the rate and quantity of spill. It also might allow the cellular material to b applied only to those compartments that are most vulnerable to

and cost.

2.2.2 Other Methods of Reducing Tanker Fire Hazards

Other techniques that are considered for achieving reduced level fire hazards from LNG tanker spills are described in the sub-sections that follow.

2.2.2.1 Gelled LNG

Experiments have demonstrated that LNG can be transformed to a g using small percentages of either water or methanol. The gels have b shown to evaporate at a slower rate (on a unit area of heat transfer surface basis) than the liquid, and it is predicted that the spreadin rate of the gel on water (on spilling from a cargo tank) would be les than that of LNG as well. The maximum size of the evaporating pool may also be reduced. It has been estimated that, because of these effects, the maximum distance that a vapor cloud might travel when ge is spilled in water would be about one-fourth that if the same amount (25,000-M^3) of LNG were spilled. The effect of gelling of LNG on haz from pool fires has not been estimated, but significant decreases mig be expected.

The achievement of large effects, however, would require gels wi higher (and perhaps excessive) percentages of gellant (H_2O or CH_3OH) have been used in the laboratory. Economical manufacturing processes also would have to be developed.

2.2.2.2 Solid LNG

Natural gas may be solidified by lowering the temperature to its freezing point. Shipping of natural gas in solid form would be expec to reduce the quantity and rate of spillage, but it would require maj changes in the processing of natural gas at the export terminal and i the design of ship containers as well. No experiments to form solid natural gas large enough to assess its structural characteristics hav been reported, nor have methods of manufacturing and transporting it

:y solution.

2.2.2.3 Methanol

The conversion of methane, the primary component of natural gas, ethanol has been considered in the past as a means of reducing the of transportation. Methanol could be shipped in slightly modified ·entional (crude oil) tankers, which are much less costly than LNG ›s. The savings in transportation, however is not large enough to ›ensate for the increased costs associated with energy losses in-red in the conversion of natural gas to methanol and the later trans mation of methanol back to a synthesis gas. This trade off also become less attractive as the result of the increases in gas prices t have been experienced in recent years.

Methanol would be safer to transport. It is miscible with water l when spilled, would disperse in water quite rapidly to the point ere the resultant mixture would no longer be flammable. Methanol al s a relatively low vapor pressure so that vapor cloud hazards would greatly diminished. Large quantities spilled and mixed with water uld adversely affect the aquatic environment, however.

The methanol approach, then, offers the opportunity of achieving ıfer transport, but at an increased cost. This would probably be rue even if markets were developed for the direct use of methanol an he costly reconversion to synthesis gas were to be eliminated. Howe f the cost of LNG tankers were to be increased for safety reasons, t ethanol route might become more attractive, particularly for project equiring long shipping distances. The implementation of a methanol mport project would require a large capital investment, some risk, ın extended period of time before it could be put in operation.

2.2.2.4 Flame Suppressants

In concept, extinguishants, such as halons, could be mixed with LNG and render it non-flammable. In practice, however, excessive amounts would be required. Uniform mixtures of the suppressant and

might result in trace (but hazardous) quantities being presen gas send-out. This concept is considered impractical.

2.2.3 System Costs

Generally speaking, improvements in safety are accompani creased costs, and this appears to be true for all of the LNG reduction concepts that have been reviewed in this study. In liminary evaluation we consider very approximate indicators o benefits so as to identify areas of potential interest and to totally infeasible concepts.

As an indicator of hazard reduction (benefits) that may with one or more approaches, we assume that the best that mig is that equivalent to the effect of the previously mentioned spill over a period of 30 minutes.

For a cost baseline, we have used the costs associated w what typical LNG project consisting of a billion standard cub per day project, with the LNG shipped from Algeria to Texas. line costs are shown in Table 2.

Using this baseline, we estimate that the cost of gas a might be increased by as much as 1 percent of the total (some for tank partitioning and for multi-tank vessel concepts. A less than 0.5 of 1 percent increase might be reasonable for involving the hanging wall of expanded metal used to impede of LNG.

Since industrial processes for making gelled or solid L quantity have not been developed, the costs associated with cepts are more uncertain than the above methods for reducing and quantity of spill. However, assuming that new and uniqu would have to be built for both concepts, and new ship desig terminal facilities developed for solid LNG, the incremental in cost of gas might be as much as 15 percent for the gelled somewhat more than this for solid LNG.

TABLE 2.2

ESTIMATE OF COSTS FOR

LIQUEFYING, TRANSPORTING, AND REGASIFYING LNG

(ARZEW, ALGERIA TO TEXAS)

1 BSCF/Day

		Cost in Dollars	Percent of Total Cost	
Cost of Gas		$0.50/M SCF		.18
Liquefaction				
Fuel	.075		.027	
Operating Costs	.103		.037	
Capital Charges	.662	.84	.240	.30
Shipping				
Fuel	.030		.011	
Boil-Off	.092		.033	
Capital Charges (vessel)	.790		.286	
Fixed Costs	.225	1.137	.081	.41
Receipt and Regasification		.285		.10
TOTAL		2.762/M SCF		1.00

attainable by transporting methanol instead of LNG might require as much as a 10 percent, or more, increase in cost per unit of energy delivered.

The economic impact of cost increases of the magnitude present here will also require considerable analysis. One perspective, how is to compare the potential reduction in monetary loss attainable b significant improvements in safety with the cost of employing these improvements. If, for example, one were to assume that a hazard-reduction concept could achieve a decrease in the total losses that might occur in a single major accident of $100 million (including property loss plus losses associated with the ship itself), and if is further assumed that the yearly probability of such an accident occurring is unusually large, say of the order of 1 chance in a 100 per year, then the prorated yearly savings would be about $100,000. Clearly, the hazard reduction concepts considered here would greatl exceed this value and, on this basis alone, might not be considered to be cost-effective.

This, however, does not consider the indeterminate value of lo associated with injuries and fatalities that might result from a ma accident nor does it take into account the possibility that the ove impact of the incremental increase in cost of gas might be consider be low relative to the potential benefits.

.3 VULNERABILITY OF LNG TANKERS AND CREWS TO FIRES

2.3.1 Vulnerability of Ship and Crew

Most of the published work on the safety of LNG tankers has centere n hazards presented to personnel and property external to the tanker tself. However, a large pool fire from a 25,000-M^3 spill of LNG might ause extensive damage to the ship and either severely or fatally injur he crew as well. The fire exposure might either directly or indirectl ause failures of cargo tanks that are not damaged in the initial phase of the accident and, at the very least, may result in a severely damage and immobile vessel with no trained crew to assist in its salvage.

A prelimiary review of the vulnerability of ship components to fi from a large LNG spill indicates that fire exposure may cause the hull plates to buckle or warp, or perhaps rupture the external protection c the cargo containers and compromise their insulation. Piping, deck machinery, life boats, and communication and navigation equipment may severely damaged and glass windows may be destroyed during the early phases of such an exposure. If the latter occurs, hot gases may ente certain areas and adversely affect the ship's controls.

On existing tankers, most, if not all, of the critical locations for the ship's operations may be exposed to the thermal effects of fi This includes positions within enclosures, but which become vulnerabl due to hot gases entering through window openings, as well as expose locations on deck.

2.3.2 Protection of Ship and Crew

Thermal insulation offers an opportunity to reduce greatly the critical damage caused by fire. Water deluge systems would also pro protection, but the reliability of pumps and water distribution syst is questionable, particularly if the ship were severely damaged in collision. Protecting the hull would be extremely difficult, but thermal damage to an unprotected hull would not be expected to be g enough to cause the ship to sink. The cargo tank covers, piping, c enclosures (including windows), and other equipment could, at least

case of protective enclosures for crew members, special insul
be required. On the basis of a conservative criterion that l
must be maintained at 100°F or lower for exposure to a fire o
special insulative coatings of the intumescent and/or transpi
cooling type would be required. Laboratory-tested coatings t
adequate for these purposes are available.

.4.1 Salvage and Disposal

'ast shipping accidents with other cargos indicate that possibly the ıing cargo would have to be off-loaded from a severely damaged LNG · at some location other than a loading or unloading terminal. : the tanker would be incapable of being moved to a terminal or moved may be deemed to be too hazardous.

Currently, no satisfactory method exists for off-loading cargo from ankers other than at terminals. Therefore, equipment and procedures ıch an operation would have to be developed. In this study we have dered the transfer of cargo to other ships, the disposal of cargo by flares or combustors aboard ship, and eventual disposal after the ca een transferred by pipeline to some location external to the vessel.

The transfer of cargo to another carrier during an emergency does :epresent a very likely solution, since it would be rare for another ɜl to be available and close enough to effect the transfer within the t interval of time (several days) as demanded by the urgency of the ation. Burning the LNG on board the tanker at the high rates needed mpty the ship in a short time would be difficult, if not impossible, ccomplish with flares, because of the potential thermal damage that d be effected by the large flames. Combustion equipment that would 'ide for burning aboard ship with little or no thermal hazard cannot ıccommodated aboard existing ships, and would occupy excessive space ıew tankers.

The transfer of cargo to platforms located at an appropriate distanc n the damaged tanker, however, offers an opportunity of burning LNG high rates without endangering the LNG carrier. A matrix of small res, or a series of waste heat boilers, mounted on a barge might be d for disposal. The development of flexible metal hoses for trans-·ring the LNG from the ship to the barges at a distance represents a ·midable undertaking, but appears to be feasible.

on the water at an adequate distance from the tanker. This would eliminate the need for barges and associated burner equipment to be continuously on standby at each port. Controlled pool burning of the LNG could be accomplished satisfactorily if a location could be found in which thermal hazards would not endanger nearby property.

2.4.2 Contingency Planning

Appropriate and timely responses to LNG tanker accidents may prev the escalation of the consequences of an accident. Contingency planni is necessary to achieve proper response and to conserve labor and fun in carrying out any plan. In this report, requirements for contingen planning for major LNG tanker accidents are considered, and primary inputs to these plans are discussed.

3.0 CONCLUSIONS AND RECOMMENDATIONS

(To be completed)

4.1 REDUCTION IN LNG FIRE HAZARDS

4.1.1 Introduction

Potential methods of reducing the hazards (or consequences) of L
tanker accidents depend upon:

- reducing the rate and/or quantity of the LNG that is discharg
- modifying the cargo so that the emission rate of flammable va from the spilled liquid is lowered, or even perhaps
- rendering the liquid non-combustible during transit.

To provide a basis for establishing how much different methods might ameliorate fire hazards, we have to estimate the reduction in (a) the thermal radiation from LNG pool fires and (b) the size and maximum travel of unignited vapor clouds. Although these estimates apply to hazard reduction methods that serve to decrease the rate and quantity of LNG discharged in an accident, they may, by inference, aid in evaluating other methods as well.

In this analysis, spill sizes of from 1,000 to 50,000 m^3 and spi durations of from "instantaneous" (very rapid spills) to 30 minutes a considered. The range of conditions for which the estimates are made are presented in Figure 4.4.1.

Also, as is noted in the following discussions specific relation ships are developed in this work for both pool fires and vapor dis- persion so as to accommodate extended spill times and to differentiat between the effects of rapid spills and longer-term "continuous" rele

4.1.2 LNG Pool Fires

4.1.2.1 Classification of Spills into Instantaneous and Continuous Categories

One of the principal difficulties in estimating the distances o which thermal radiation hazards from burning pools of LNG exist lies estimating the dimensions, or size, of the spreading pool of spilled liqiid. Spread models exist for the idealized "instantaneous" (very

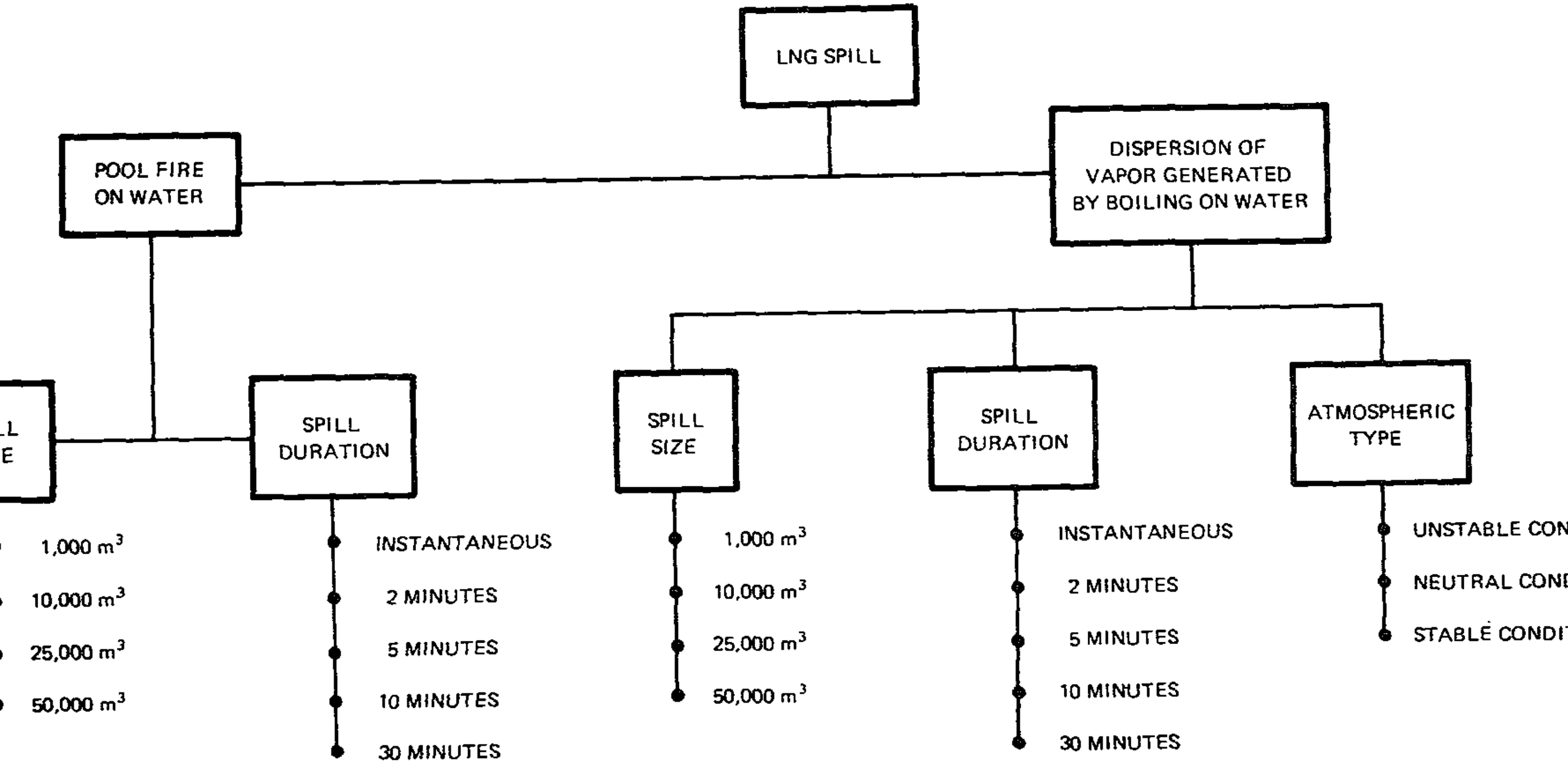


FIGURE 4.1 TYPES AND MAGNITUDES OF HAZARDS

Since no spill is truly instantaneous, it is important to establish when the spill duration might be short enough for the spill to be considered as occurring instantaneously.

This question has been addressed in Appendix A, and a time criter (cross-over spill times) has been obtained for spill durations that ma be considered as being short enough for the spill to be represented as occurring instantaneously. For spill durations longer than the cross-over time, continuous spill models are used. Table 4.1 shows the val the cross-over times for various spill sizes. The table shows, for example, that a two-minute spill of 50,000 m^3 may be considered as an instantaneous spill, whereas two-minute spills of smaller quantities a more representative of continuous discharges.

4.1.2.2. Analytical Models for Thermal Radiation Hazards

The basic relationships used in estimating thermal radiation haza are those developed in Reference 1. They consist of the following:

The maximum spread radius is represented by

$$R = \left[\frac{V^3 g\Delta}{\dot{y}^2}\right]^{1/8} \quad \text{for INSTANTANEOUS spill}$$

$$R = \left[\frac{V}{\pi t_s \dot{y}}\right]^{1/2} \quad \text{for CONTINUOUS spill}$$

The height of fire is assumed to be three times the diameter of the burning pool, and the emissive power of the LNG fire is estimated to 100 kW/m^2.

The hazard distance to skin burn injury is estimated on the basis of a skin burn criterion of 5 kW/m^2. While other criteria exist,[1]

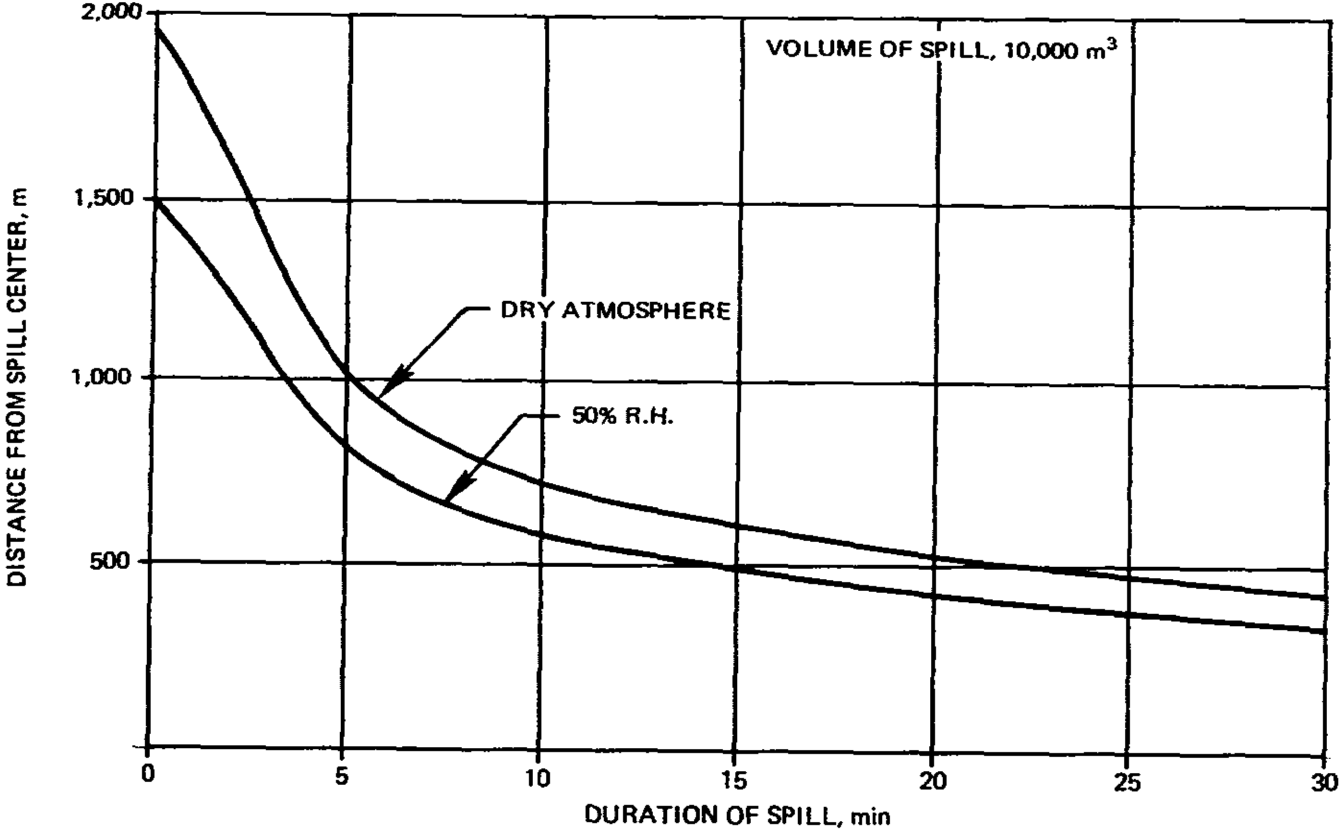
(1) Raj, P. K., "Calculations of Thermal Radiation Hazards from LNG Fires--A Review of the State of the Art," Paper #2, Session 18, Presented at the AGA Transmission Conference, St. Louis, MO., May 1977.

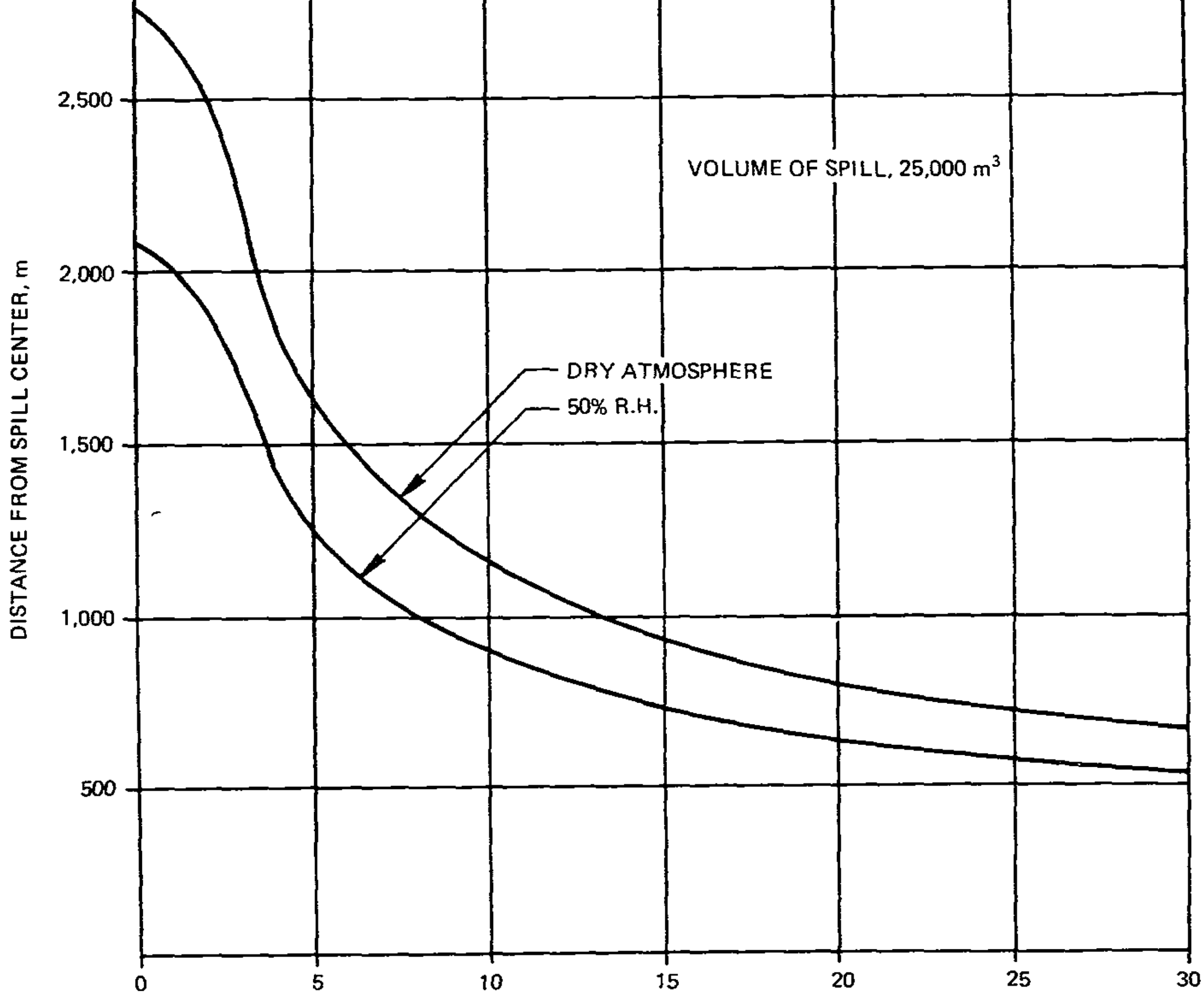
TABLE 4.1

CROSS-OVER TIMES FOR VARIOUS SPILL SIZES

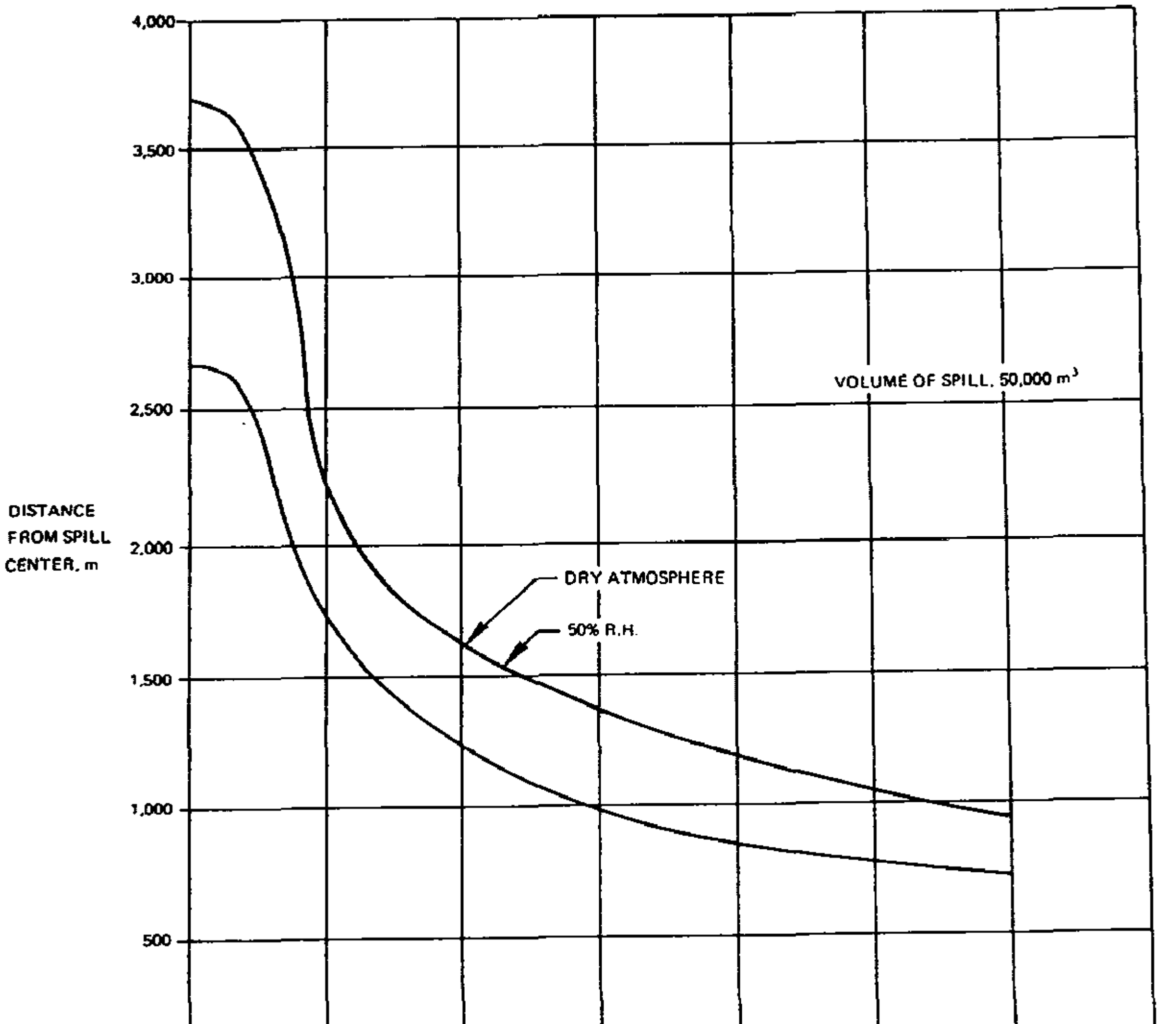
Volume of LNG Spill (m^3)	Cross-over time* (sec)
1,000	31
10,000	68
25,000	92
50,000	116

* If the duration of spill is longer than the cross-over time, the spill is to be modeled as a continuous spill.


VOLUME OF SPILL, 10,000 m3
DRY ATMOSPHERE
50% R.H.
DISTANCE FROM SPILL CENTER, m
2,000
1,500
1,000
500
0
5
10
15
20
25
30
DURATION OF SPILL, min



VOLUME OF SPILL, 25,000 m3
DRY ATMOSPHERE
50% R.H.
DISTANCE FROM SPILL CENTER, m
2,500
2,000
1,500
1,000
500
0
5
10
15
20
25
30



DISTANCE
FROM SPILL
CENTER, m
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
VOLUME OF SPILL, 50,000 m³
DRY ATMOSPHERE
50% R.H.

A vapor gravity spread model had to be developed, however, for slower (continuous) releases, as described in Appendix B. In this model it assumed that the vapor spreads in the lateral direction only and is diluted by air entrainment. The gravitational spread is terminated (somewhat arbitrarily because of lack of any other relevant criterion when the spread velocity is equal to or less than the prevailing wind speed.

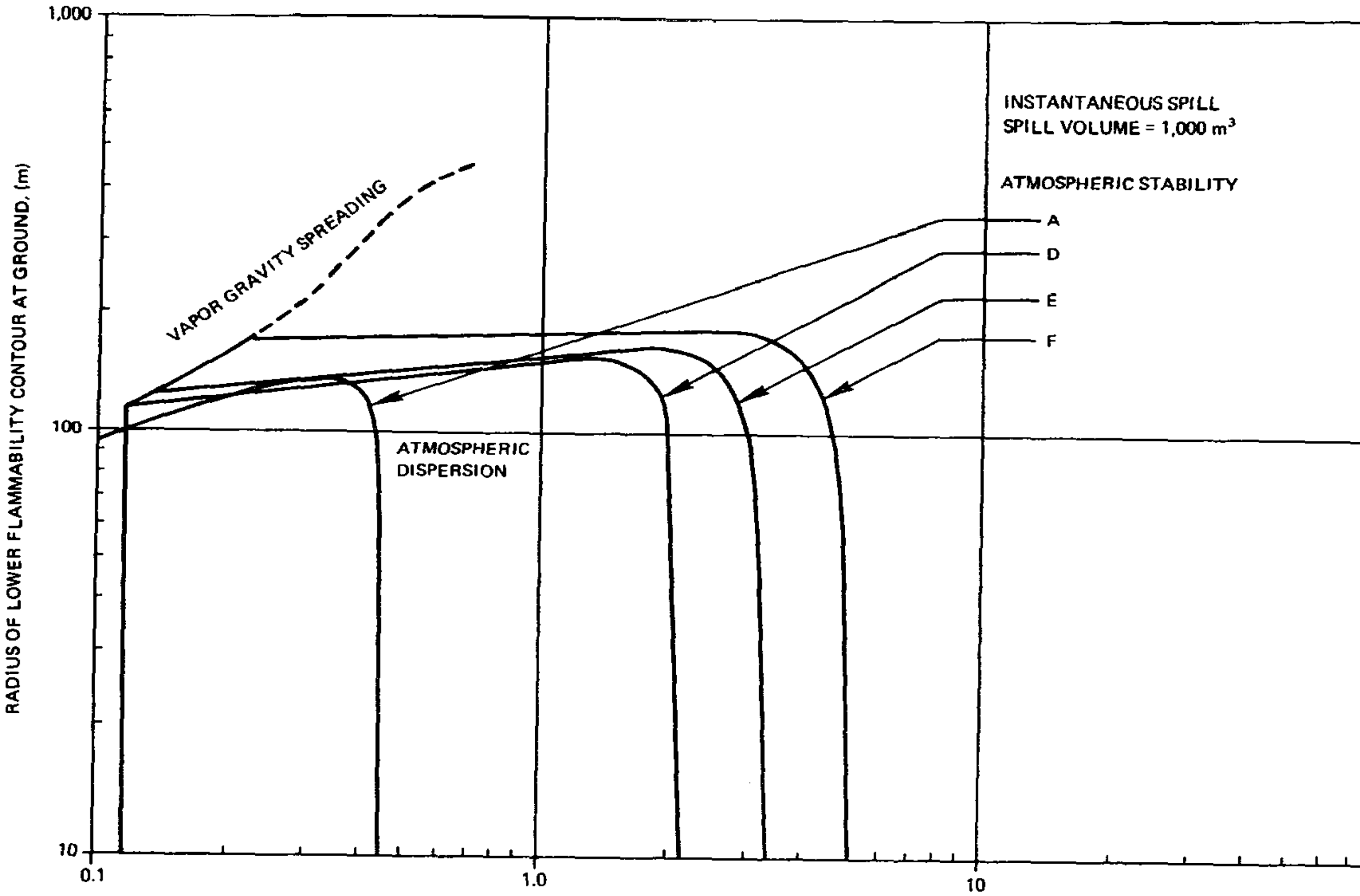
The subsequent vapor dispersion is analyzed using the convention Pasquill Gifford dispersion models. However, the vapor dispersion is modeled as if the vapors were issuing from a virtual source. The location of the virtual source is determined by matching the vapor concentration at the end of the gravity spread with the concentration vapor at the same location obtained from a conventional dispersion mo (with the source being the virtual source).

4.1.3.2 Results

The dispersion results are presented in the form of semi-widths flammable region as functions of downwind distance. The atmospheric condition is used as a parameter. The results for each spill volume and type of spill (instantaneous, continuous) are shown in separate figures.

Figures 4.6 through 4.8 show the semi-width of flammable regions the instantaneous spills of 1,000-M^3, 25,000-M^3, and 50,000-M^3 spills In each figure, the gravity spread regime and turbulent dispersion regimes are clearly shown.

In Figure 4.9, the maximum downwind distance to 5% concentration is shown for different spill volumes, with the duration of spill as a parameter. The figure refers to dispersion in very stable weather conditions, i.e., in F weather with 3 m/sec wind. Figure 4.10 shows semi-widths to 5% concentration. In both figures, the results of instantaneous spill results are also indicated.


INSTANTANEOUS SPILL
SPILL VOLUME = 1,000 m³
ATMOSPHERIC STABILITY
A
D
E
F
VAPOR GRAVITY SPREADING
ATMOSPHERIC DISPERSION
RADIUS OF LOWER FLAMMABILITY CONTOUR AT GROUND, (m)
1,000
100
10
0.1
1.0
10

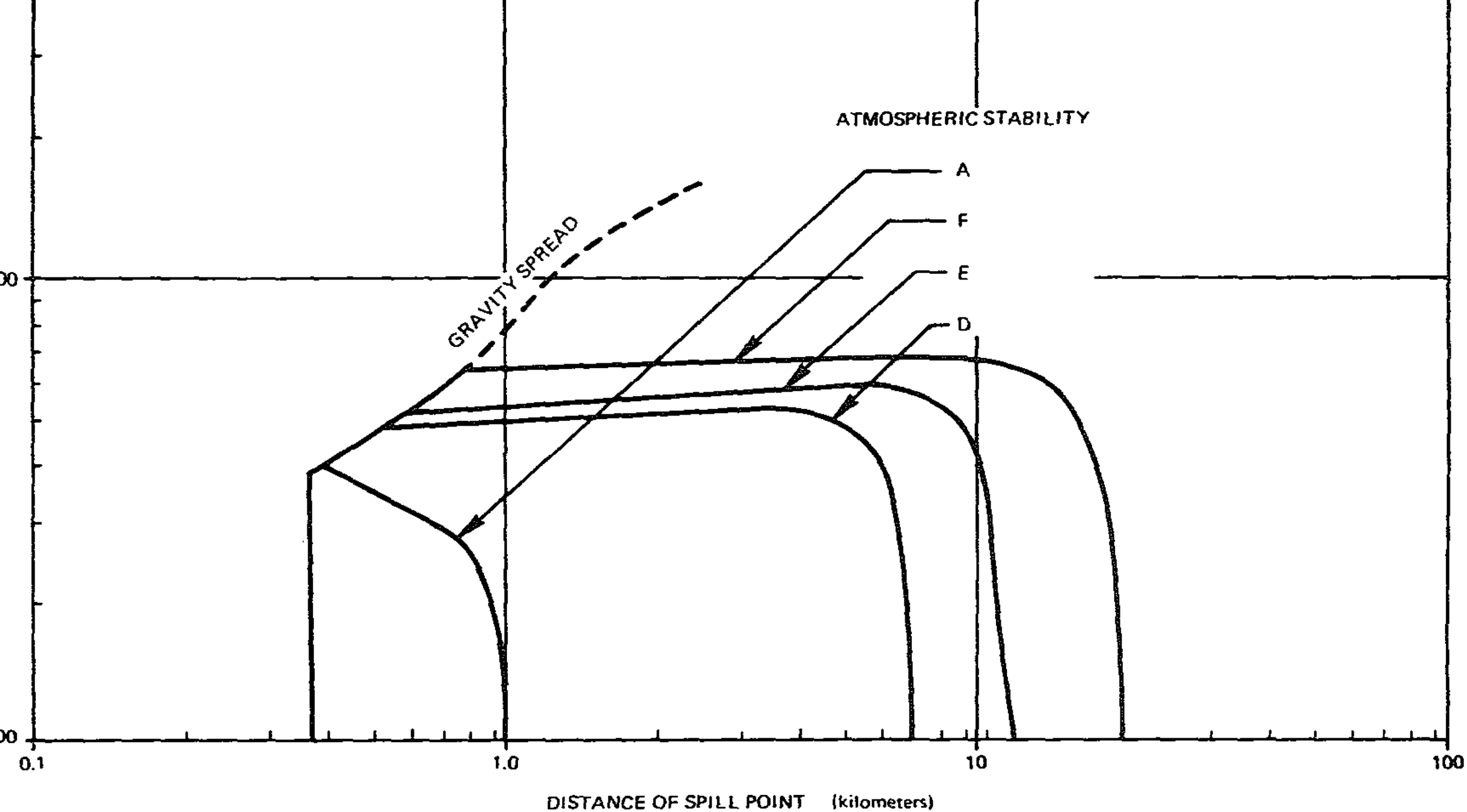
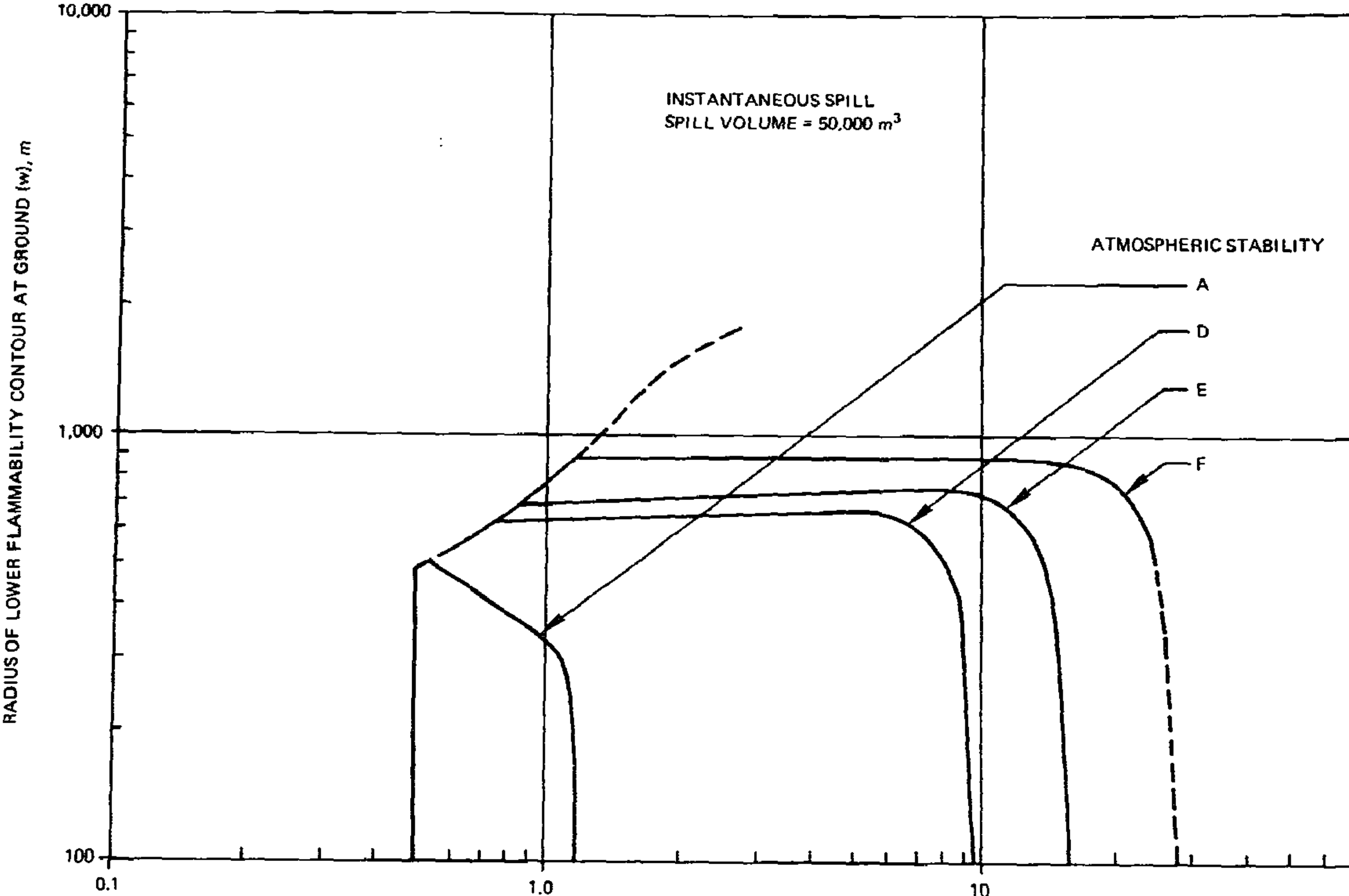


FIGURE 4.7 WIDTH OF FLAMMABLE REGION AS A FUNCTION OF DISTANCE FROM SPILL POINT FOR 25,000 m^3 LNG SPILLS ON WATER


10,000
1,000
100
0.1
1.0
10
RADIUS OF LOWER FLAMMABILITY CONTOUR AT GROUND (w), m
INSTANTANEOUS SPILL
SPILL VOLUME = 50,000 m³
ATMOSPHERIC STABILITY
A
D
E
F

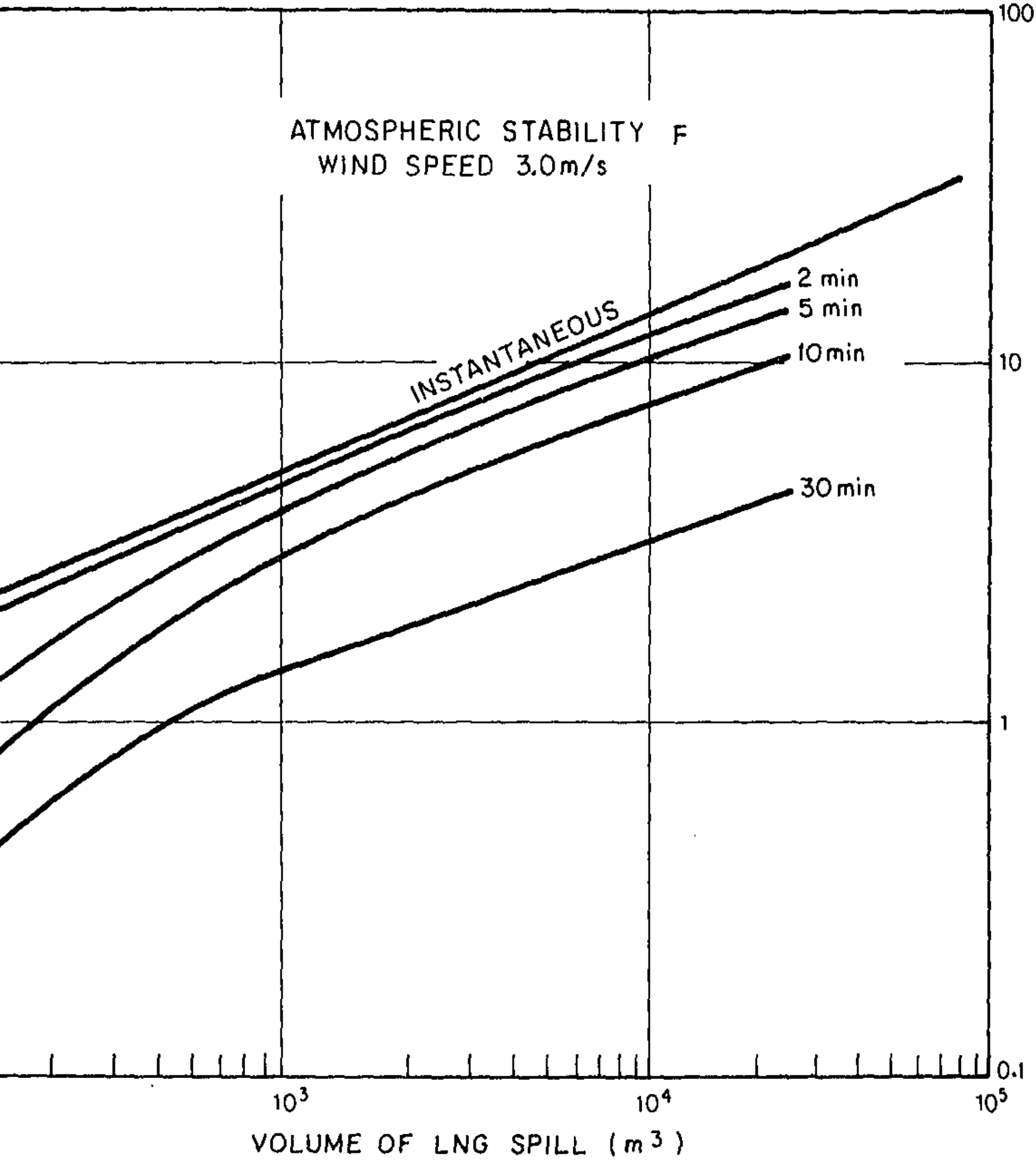


FIGURE 4.9 MAXIMUM DOWNWIND DISTANCE TO 5% CONCENTRATION vs. SPILL VOLUME.

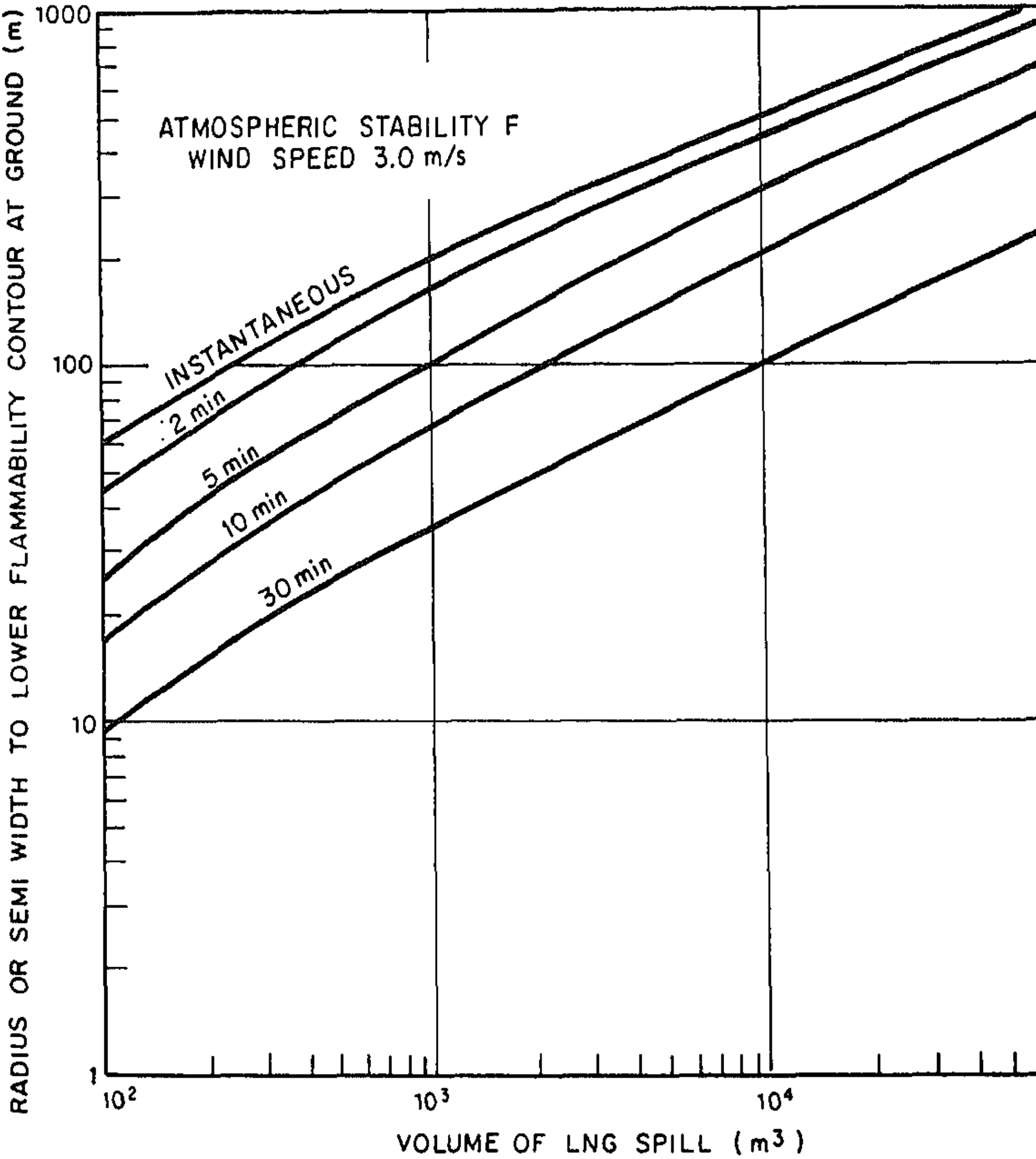


FIGURE 4.10 MAXIMUM SEMI WIDTH OF CLOUD TO 5% CONCENTRATION vs SPILL VOLUME

ures 4.9 and 4.10 indicate that the extent of the hazard (mea- total ground area of concentration above 5% LFL) diminishes with in the duration of the spill. This is what one would expect vely in developing the curves shown in Figures 4.9 and 4.10; the spreading of vapor and its subsequent atmospheric dispersion were ed <u>in toto</u> in the case of instantaneous spill. The effects of nsfer to the cloud from the water surface and the effect of ric humidity were taken into consideration. However, in the continuous release spills, the computation of maximum downwind to LFL and the width of the maximum lateral hazard extent were tially using the gravity spread model developed in Appendix B.* ately, the results were not only against the intuitive estimates, indicated some peculiarities, such as a 30-minute release idth being the same as that from an instantaneous spill of the same f liquid. The curves indicated for continuous spills in Figures 4.10 have, therefore, been obtained by first considering releases low volumes and analysing the dispersion of these vapors from ll spills with conventional dispersion models. Vapors from lume spills (100 M^3, 1000 M^3), especially those that are spilled nificant durations (more than five minutes) have very little to gravity spread. The behavior of vapors from larger spill were extrapolated from the results of 100 M^3 and 1000 M^3, but dance from the gravity spread model (Appendix B) as to the variation e. Therefore, it is coutioned that by merely exercising the model Appendix B, the results indicated in Figures 4.9 and 4.10 cannot ned. They are based partly on the gravity spread model, partly ntional dispersion model and engineering judgment.

results indicated for the downwind hazard extent for the case of us spills are only approximate. Improved results can be obtained ying the vapor gravity spread model to include the ground heat and the heat of water vapor condensation. The instantaneous sults, however, would not be expected to vary with these changes.

recalled that this model is approximate and does not include the ts of heat transfer and of the atmospheric humidity.

g	=	acceleration due to gravity	(m/sec^2)
L	=	characteristic length scale ($V^{1/3}$)	(m)
R	=	maximum spread radius	(m)
t_{ch}	=	characteristic time - L/y	(s)
$t_{cross\text{-}over}$	=	cross-over time for change in type of spill	(s)
t_s	=	duration of spill	(s)
V	=	volume of liquid spilled	(m^3)
$\dot{y}$	=	liquid regression rate (volume boiling per unit area per unit time)	(m/s)

GREEK

Δ	=	density defect $(1 - \frac{\rho_{liq}}{\rho_{water}})$	
ρ_{liq}	=	liquid density	kg/m^3
ρ_{water}	=	water density	kg/m^3
ξ	=	dimensionless radius of spread	
τ	=	dimensionless time	

0 VULNERABILITY OF LNG TANKERS AND CREW TO FIRES

(To be completed)

An additional factor in reducing the overall consequences of an LNG tanker accident is the emergency removal of cargo from the vessel when it is unable to unload at its designated receiving terminal, either because it is immobile or it is deemed to be unsafe to do so. It is most likely that in any LNG tanker accident - from the mildest failure to the severest impact (e.g., a collision) - a major portion of the carg will remain on board after the initial event has taken place. If, for some reason, the ship cannot then proceed to its unloading terminal, this large quantity of fuel may present some level of danger to populate areas, shipping, and to those charged with managing the damaged vessel. Emergency off-loading, if it can be conducted in a reasonably safe and timely manner, may very significantly reduce the overall risks presente by a disabled tanker.

Studies of potential collisions of LNG tankers with other ships have shown that only those LNG tanks that are in the direct path of the impacting ship may be damaged sufficiently to release their contents. Hence, only one or two tanks, at the most, out of the usual five for the large 125,000 M^3 vessels might lose their contents under the most severe of credible events. Although there have been no such accidents with LNG vessels, a considerable number of examples of accidents involv other types of tankers do exist. The collision of an LPG carrier (Yuyo Maru) in Tokyo Bay resulted in the loss of its secondary cargo and a large fire. The LPG containers, however, retained their integrity so that the disabled ship with its LPG cargo presented, at least, a large (perceived) threat to nearby populated areas. It took several days and created considerable anxiety before a successful solution was implement (which, in this case, resulted in the destruction of the ship in a remo location). Oil tankers also typically retain much of their cargo after a major accident, as, for example, was the case with the Torrey Canyon and the Argo Merchant. In both instances, large quantities of oil remained on board immediately after the initial incident. If the cargo

on of the sea could have been prevented.

date there has been little or no analysis made, or at least le, in the literature of the salvage problem for LNG tankers. s of the risks of tanker accidents has not been carried out in ent detail to provide an adequate base for designing or evaluating t/effectiveness of salvage concepts, nor have potential methods vage or disposal been delineated or evaluated. To our knowledge, or no response planning dealing with LNG tanker accidents has rformed to date.

this study a preliminary review is made of the conditions that arrant salvage or disposal of the LNG cargo, potential salvage , and response planning. Emphasis is placed on salvage or dis- oncepts.

6.2.1 General Considerations

The events that might lead to the necessity of removing cargo fr a disabled vessel are expected to be rare. Such events would require that a vessel present either too great a hazard to be unloaded at its designated receiving terminal or, for some reason (e.g., too large a draft caused by flooding), that it actually be unable to proceed to t terminal on its own. They represent major system failures for which unprecedented measures to mitigate against them have already been taken.

Nevertheless, accidents are possible and, given the potential threat of the cargo that may remain on a ship after an accident has occurred, it is only prudent to consider methods of eliminating the hazards presented by a damaged or disabled vessel.

A complete examination of the events that may result in a ship n being able to off-load at the receiving terminal and of the various conditions of the vessel that may influence emergency off-loading procedures would require a formalized failure analysis in which such techniques as failure modes and effects analysis, fault trees, and ev trees, would be utilized. Here, however, in this preliminary survey, only generic failure modes and primary effects of the failures are considered. This provides a base on which the essential needs of salvage or disposal systems may be considered, and on which prelimina emergency response plans may be developed. This study, however, does not provide information in sufficient detail to design these systems, nor to completely evaluate their cost/effectiveness.

6.2.2 Primary Failure Modes and Causes

Primary failure modes which might individually or collectively create a hazardous situation in which salvage or disposal may have to be considered are presented in Table 6.1 and the principal causes of these failures are listed in Table 6.2. Attempts have been made to estimate the probability of occurrence of some or most of these cause

Table 6.1

PRIMARY FAILURE MODES

Control Failures

- Steering
- Propulsion
- Navigation
- Ballasting
- Cargo monitoring and transfer system

Electrical Power Failures

- Electrical distribution failure
- Alternator/generator failure

Propulsion Failures

- Prime-mover failure
- Fuel deficiency
- Drive train damage

Crew Failures

- Absence
- Incapacitation

Containment Failures

- Insulation failure
- Leak in primary barrier
- Leak in primary and secondary barriers
- Leak in vapor transfer system
- Catastrophic failure of one or more containers

Vessel Structural Failure

- Damage of free-standing container supports
- Perforation of two hulls with flooding

PRIMARY CAUSES

Internal Abnormal Events

Operating/maintenance deficiencies
Equipment/materials deficiencies
Internally caused fires or explosions
Illness/injury to crew
Inadequate crew training and/or information

External Abnormal Events

Collision
Grounding
Ramming
Sabotage/vandalism
Aircraft/missile impact

Other More Rare Events

Meteorite impact, tsunami, and tornado

ns present the greatest (although very small) risk of a major
cident.

.3 The Need for Emergency Off-Loading

the various possible accidents, grounding and/or structural are probably most likely to require emergency off-loading of

t shipping experience shows that it is possible for an LNG o run aground, although its occurrence might be quite rare due xtra precautions taken by the operators, the high level of ce of the crew, improved navigation systems, and the extra- control exercised by the U.S. Coast Guard. Groundings might e to combinations of events such as the simultaneous loss of and propulsion controls, the occurrence of a severe wind d a propulsion failure, and the failure of navigation, along ere maneuvers taken to avoid a collision.

oundings unaccompanied by collisions, rammings, or other events may, in the majority of instances merely require that either by itself or with assistance be refloated, perhaps at or several high tides later. In some instances, however, the ng of the vessel may be difficult and time-consuming. The of off-loading some of the cargo to lighten the vessel, along real or perceived urgency to remove the potential threat of a y be sufficient to require some discharge of cargo within a ely short-time after the incident.

a major structural failure, accompanied by a massive spill of re to occur, as in a very exceptional collision, a large fire ost likely take place severely damaging and disabling the ship. ainers not in the direct path of the impact might maintain tegrity, and thus, very large quantities of LNG might remain on aged ship. Depending on the damage assessment made after the been brought under control, a decision that it might be prudent load the remaining cargo at a safe location might be made.

The structural damage of a ship in a grounding, ramming, or collision, for example, could jeopardize the LNG container by weakening the suppo ing structure, the bottom of a membrane, or some free-standing tanks, or even the spheres of the Kvaerner-Moss ships. Assessment of the damage might indicate that movement of the vessel to a pier or wharf at the receiving terminal might be too risky. Instead it may be decid that the cargo should be off-loaded at a remote and relatively safe location. A potential inability to assess damage adequately may also lead to the same decision.

Other structural damage might involve loss of insulation, failure of primary and secondary LNG containment barriers where damage assess- ment may be difficult, and fires or explosions aboard ship. In some c these instances, it may also be wise to off-load at a safe location.

A major failure at the receiving terminal during a ship-to-shore operation might, also, in some way damage the LNG vessel so that it would have to be removed to a safe location for cargo off-loading.

As in most emergencies, the sooner the threat can be remove less the risk. The emergency removal of cargo from an LNG vesse ever, will be time-consuming. It is more than likely that emerg off-loadings of entire cargo will greatly exceed the 10 hours or that is required during normal ship-to-shore operations. Added time for transfer will be the movement of the ship to a safer lo (if it is not grounded), the delivery of unloading equipment at site, and the rigging of the equipment. Hence, it might take se days to unload cargo from a disabled ship.

If the off-loading is to be accomplished when the ship is g at a location near to a populated area, the urgency of the opera may be much greater. Given that such a condition is credible, t will be a major need to remove cargo as quickly as possible. As current technological limitations, this might be of the order of or more.

Another case may involve a ship that is so badly damaged th deemed too risky to remove the remaining cargo. If such a case the authority in charge might order that the ship be towed to se destroyed. This is a drastic measure, and it is conceivable tha might be completely avoided if proper salvage and disposal plans procedures are developed and made available prior to the inciden

off-load cargo from an LNG tanker are presented in Table 6.3. The failure modes listed serve as the basis for identifying and evaluating emergency off-loading systems and procedures.

Table 6.3

ACCIDENTS REQUIRING EMERGENCY LNG OFF-LOADING

Accident Type	General Location at Off-Loading	Earliest Off-Loading Need after Incident
(1) Grounding		
• Partial off-loading (no damage, but need to lighten ship)	At site of grounding	< day
• Complete off-loading (ship damage severe; too risky to move loaded ship)	At site of grounding	< day
(2) Structural Damage (complete Off-Loading)		
• Severe damage, including a release of LNG	Remote area or at sea	> day
• LNG containment in jeopardy, but no spill	Remote area or at sea	> day
• LNG containment may be in jeopardy, but unable to assess damage	Remote area or at sea	> day
(3) Receiving Terminal Failure		
• LNG tanker undamaged	At a secondary receiving terminal	Several days
	[illegible] at sea	> day

Salvage or disposal of the cargo implies that it is removed fro the ship under abnormal conditions and usually during an emergency. conditions under which salvage or disposal may be required can range from off-loading at a terminal when there is a major systems failure to the removal of cargo from a damaged immobile ship located near a populated area.

Major systems failures that might cause emergency conditions at terminal off-loadings include, for example, loss of ship power witho provision for shoreside electrical connections, damaged transfer li and loss of transfer monitoring systems. Most of these problems and the hazards associated with them can be taken care of with adequate contingency planning and provision for equipment and skills necessa to solve them.

In this study we focussed on the more difficult problems assoc with cargo disposal when the ship either cannot be berthed at a ter or it is deemed unsafe to do so. In addition, we considered generi problems common to the 125,000-M^3 vessels. Details of design and o erational procedures were left for further study.

In this chapter, we consider the potential off-loading rates a their implications, existing methods of removing cargo, problems wi getting LNG out of the shipborne containers and working with a dis-abled ship, and potential methods of cargo removal.

6.5.2 Rate of Disposal

Table 6.3 indicates that emergency off-loading times required t remove a perceived threat may vary from less than a day to perhaps days, depending upon the type of accident and the resulting failure The shortest possible time, of course, is that determined by the pu capacity of the on-board immersion pumps. The longest period of ti

ined by those in charge of salvage.

rates of discharge and the hazards resulting from the release
IG at these rates for different total discharge times are pre-
Table 2.1 of the Summary section of this report. These data
n indication of the potential hazards from jetting liquid,
aporized cargo, and flaring, as well as from failed lines
ergency transfer.

3 Removal of Cargo from Shipborne Containers

3.1 Pumping of Cargo

shipborne LNG cargo tank systems use submerged cryogenic pumps
arging LNG at the receiving terminal. The pumps are submerged
net positive suction head can be maintained. Since the LNG
ned at near atmospheric pressure, it is not possible to transfer
ith pumps located external to the tanks.

e electrically driven pumps constitute the sole method of
the tank. There are no bottom penetrations that would allow
of the tanks by gravity, nor generally can the tanks be
y pressurized to force cargo out of the top discharge lines.

rive the cargo from the tanks by gas pressure requires a
of about 0.195 psi per foot of tank height (62.4 x 0.45/144).
0-foot deep prismatic tank would require 17.55 psi plus the
to overcome friction and flow losses. A 120-foot diameter
uld require 23.4 psi of pressure minimum. The spherical tanks
stressed to this degree in case of emergency, but no other
containment system can accept this type of loading. It is
t the safety valves are set at 3 psi on at least some spherical
ems. They cannot be reset remotely, and it may be very diffi-
not impossible, to set them at higher values under emergency
s.

a 3 psi permissible overpressure, LNG could be lifted about
above the liquid surface, which would allow very little of the

10 psig, for example, some 50 feet of cargo depth could be removed, which is about 43 percent of the total tank depth and corresponds to about 45 percent of the cargo volume.

Partial emptying (or loading) of an LNG tank does not necessarily improve the safety of the situation. In fact, the membrane tanks must be operated under normal conditions within the under 5% or over 95% full range, due to problems stemming from sloshing loads in the intermediate range. The self-supporting tanks are less susceptible to the hazards of these dynamic loads; the spherical tanks present different geometries and may be operated in the 10% to 90% range.

The most difficult problem with achieving cargo discharge during an emergency may be the loss of power to the submerged pumps. Typicall each tank on a 125,000-M^3 vessel has two 300-HP submerged pumps. The power requirements, then, are relatively large and would require exceptional sources of power to supply the needed energy. Facility is provided in all ships for pump replacement.

6.5.3.2 Ship Transfer Lines

In present ship designs, the discharge lines from the storage tanks are manifolded, and discharge is made at one or more flanges amidship. An articulated (e.g., CHIKSAN) system located on shore is connected to this flange at the time of off-loading. Some ships can off-load on either side while others are designed for connections to be made to only one side of the ship. Redundant shipborne transfer systems are not usually provided.

In an accident, the transfer lines, manifolds, valves, and/or con trols may be damaged so that major components may have to be replaced before off-loading could proceed. Once this is done, then a system must be provided to transfer the LNG to another vessel or to a vent, flare, or combustion system external to the ship (that is, if the LNG is not to be jettisoned or either vented or flared from the ship itsel

tion of both. Ship-contained flexible metallic lines were employed for off-loading cargo from the LNG barge MASSACHUSETTS, while most s use a shore-based articulated arm arrangement. The flexible hose offers the advantage of accommodating a variety of off-loading cond whereas use of the articulated rigid-pipe system is more limited. B cause greater spans and vertical heights than are experienced in no off-loadings most probably will be required, the design of either sy would be expected to stretch the state-of-the-art and the actual devices would be very costly. In addition, special handling and suppo systems (e.g., booms and cranes) on board the ship would also be necessary. Moreover, if high rates of off-loading are to be employe vapor would have to be provided to the vessel's cargo tanks to preve the occurrence of sub-atmospheric pressure within them.

Concepts for articulated transfer lines that might be used in s to-ship transfer are shown in Figure 6.1. To provide freedom of mot a minimum of two swivel joints in the horizontal plane and four swiv joints in the vertical plane are required between the connecting fla of the two ships. If each ship carried half such a link as standard on-board equipment, each ship-set most probably would have two horizontal and three vertical swivels, as indicated in Figure 6.1. A support system from an elevated point would be required for the weig of the piping, joints, and cargo flow. Unless the systems are permanently installed on both sides of the ship, they would have to be backed up by a handling capability for shifting from side to side an to stowages and header flanges.

The lower part of Figure 6.1 shows an arrangement that is analo to the use of one CHIKSAN arm on each ship. Such a permanent arrang ment would require one arm on each side of the ship, plus permanent valving and piping to permit its use, when needed, alternatively to the normal discharge flanges. With a portable arrangement, only one unit has to be carried and it can be rigged where and when desired. However, cost analyses indicate that the expense of the kingpost an

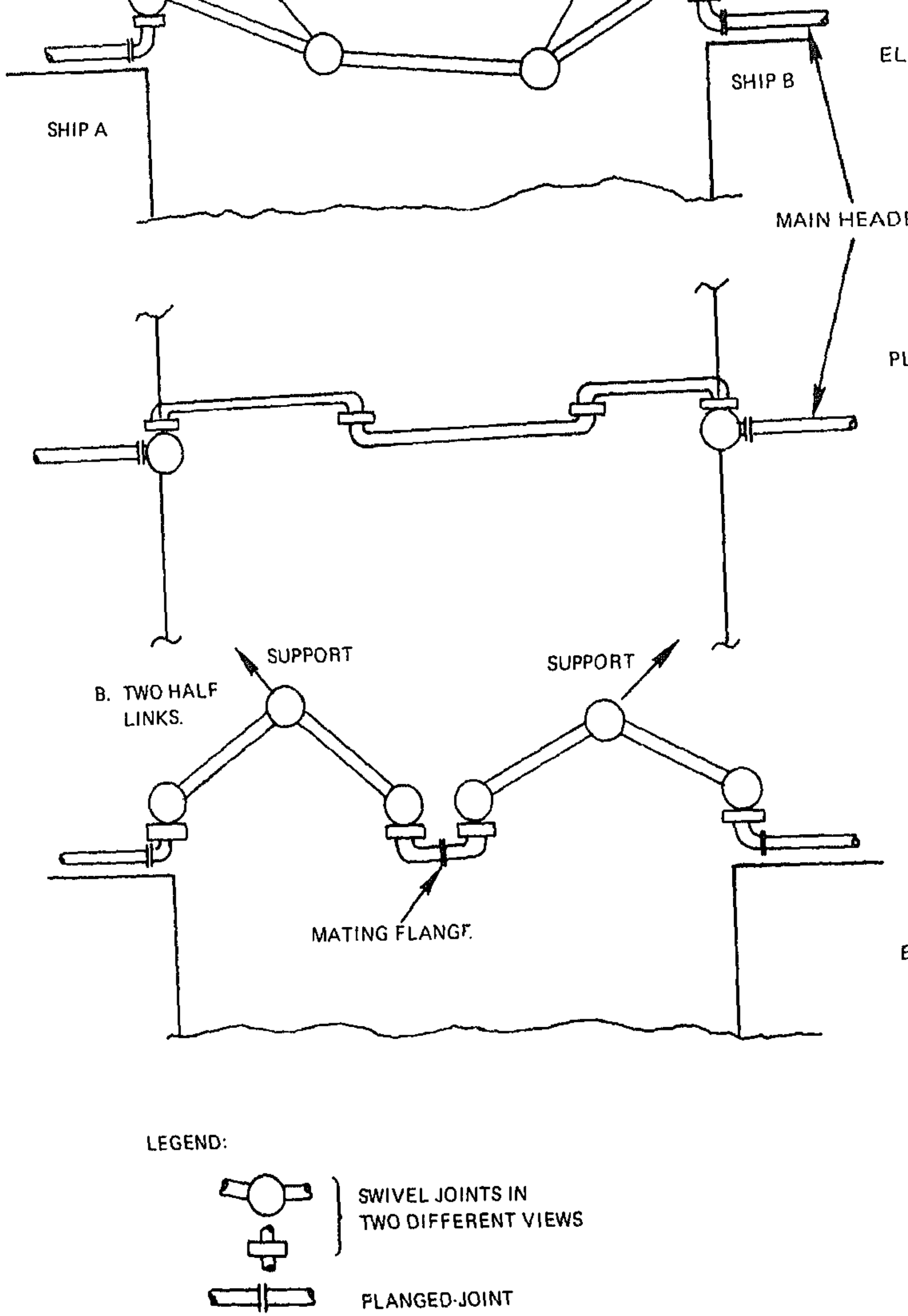


FIGURE 6.1 SCHEMATIC OF ARTICULATED TRANSFER LINK

ions. The other factor which remains somewhat unresolved at me is the outreach required, and the CHIKSAN arms are known to limited capability in this respect.

nce the entire problem under discussion deals with a rare and the equipment under consideration may rarely be used, if ne matter of cost, weight, and space is most important, and tial analysis and testing would be required before a concept e chosen and implemented.

5.4 Transfer from Damaged and Disabled Ships

badly damaged LNG tanker, as could conceivably occur as the re- it being impacted by another ship in a harbor or channel, may ecial problems in salvage or disposal of the cargo. In a collision, the entire contents of one or more of the cargo ould be spilled in a very short time. This would result xceptionally large fire with severe thermal exposure of the ship crew. Transfer lines and valves, electrical power cables, and systems might be damaged and broken and the crew might be in- ated. Furthermore, damage to the insulation and structural s of cargo tanks that remain fully loaded after the accident esult in emergency venting (with the corresponding hazard re) and a threat of further releases due to failure of one or the remaining tanks. The ship could also trim, making it dif- to gain access to the ship's deck and to work on it.

fore off-loading can be considered in a specific accident situa- thorough damage assessment would have to be made and the risks loading evaluated. Off-loading problems such as the following ave to be considered:

Adequate descriptions of the cryogenic system aboard ships. Access to sufficient information about the system might be difficult and time-consuming, unless specific measures were taken to make this information accessible to potential sal- vage personnel prior to the accident.

and implement salvage proc...

- The inability to perform any work on board while t... system is ruptured and leaking gas into the atmosp... the ship.
- The difficulty associated with raising large piece... from low lying vessels to the deck of the LNG tank... decks of the 125,000-M^3 tankers can be as high as ... more above the water line.
- Disconnecting and/or cutting large diameter insula... may contain flammable vapor and attaching new temp...
- The availability and means of providing auxiliary ... power if the tanker's electrical system is inoper...
- Providing adequate protection and emergency escap... personnel.
- Preparing for and accommodating sudden shifts in ... orientation.
- Motion of the ship.
- Fendering of salvage and other vessels.

6.5.5 Salvage and Disposal Methods

6.5.5.1 Present Off-Loading and Vapor-Handling Syst...

The design off-loading times at receiving terminals ... M^3 ships is generally of the order of 12 to 48 hours. H... rates of the order of 2,500 to 10,000 M^3/hr (11,000 to 4... are attainable under normal circumstances. Vapor must b... from the shore side to replace liquid taken from the tan... taining a positive pressure. Also, since the LNG tanker... operate at a constant draft (whether loaded with cargo c... water ballast must be pumped into ballast tanks at a rat... with the offloading of the LNG. The ballast system has ... equal to the cargo load and a volumetric capacity of abo... for a 125,000-M^3 ship would be 55,000 M^3.

0.25% per day. This is about 5,000 scf/min and is normally used for propulsion while the ship is in transit. Boil-off may also be burned in the ships' boilers when the main turbines are not in operation by use of the "steam dump" system. Current U.S. Coast Guard rules do not allow vapor to be vented to the atmosphere when the ship is in port. Emergency vents are provided, however, and they would be expected to handle somewhat in excess of the normal boil-off in the event that other vapor-handling systems fail.

6.5.5.2 Disposal from the LNG Tanker

Potential methods of removing cargo without transferring it to equipment or facilities external to the ship include venting and flaring, the use of combustors, and jettisoning overboard. Each of these methods is discussed below.

6.5.5.2.1 Venting and Flaring

The venting of vapor from vent stacks aboard ship at the high ra of discharge that might be required during an emergency is hazardous and probably impractical. There is a finite probability that vapor would be ignited by static discharge or by some other source so that in effect, venting might be considered to be similar to flaring. In addition, at high rates of venting, the unignited vapor cloud may tra far enough to endanger surrounding areas.

High rate flaring would be difficult to achieve without causing thermal damage to shipborne systems from the thermal radiation emitte by the large flames that would be produced.

A 25,000-M^3 LNG tank is the equivalent of about 503 million cubi feet of gas at ambient temperatures. To flare such a gas volume within 24 hours requires a rate of 5,800 ft^3/sec. This would release about 6.7 MM Btu/sec. Even when the flaring period is stretched out over several days, the entire design and ship protection problem remains formidable. It may be noted that the combustion of 5,800 ft is equivalent to about 10 million hp or 7.7 million kW.

Either a vent or flare system will require a vaporization s convert the liquid to gas before it is sent to the vent. Based comparison with shore-based vaporizers, the placing of an instal having a capacity of 6,000 ft^3/sec or more aboard an existing sh would appear to be difficult indeed and utilize a significant am space on a newly designed ship.

6.5.5.2.2 Combustors

An alternative which may be more attractive than flares is ment of a combustor which can be fueled directly with liquid LNG a small gasifier to provide start-up heat and pilot fuel would b essary, or normal boil-off may serve this purpose. Major weight space requirements, as well as capital investment, would be grea reduced. An installation capable of burning 17.3 M^3 of LNG per remains a major, sophisticated and expensive system. Excess air be required to eliminate the large flame developed during flarin size of the equipment again might be excessive for installation tanker.

6.5.5.2.3 Jettisoning

The jettisoning of large quantities of LNG over an extended generates specifically those hazards in inshore areas which it i sired to ameliorate. In addition, there is a finite probability the vapors would ignite and the resulting thermal effects could pardize the whole operation.

Experiments have been made with jettisoning of LNG from shi Tests were madewith the METHANE PIONEER in 1959, and more recent (1973) Shell Research Ltd. and Shell International Marine Ltd. c tests on the 75,000-M^3 GADILLA in jettisoning LNG. This latter engaged in the Indonesian trade, is designed for a port which re loading over the stern. The cargo manifolds are located on a sp projecting over the transom. A discharge nozzle was fitted and with sufficient pressure so that the LNG stream struck the wate surface well clear of the hull, which also was sluiced with wate

successful demonstration of the feasibility of the technique. The tern discharge arrangement is peculiar to this class of ship; most arge carriers discharge amidships and have no cargo installation aft f the forward bulkhead of the deckhouse, except for the gas fuel ines passing to the engine room via a double-walled conduit. The ADILLA tests demonstrated the feasibility of jettisoning LNG cargo at igh rates at sea where the vapor cloud presented a hazard to no land reas and where no danger of ignition from non-ship sources existed. ven under these conditions, however, one might question whether there ay be some probability of ignition due to static discharge or by some ther mechanism.

6.5.5.3 Ship-to-Ship Transfer

The salvage of the cargo by transferring it to another vessel has reat appeal in that it could save an expensive cargo - an estimated alue of $8 million at the terminal's sendout. The primary limitation, owever, is the availability of a cooled-down empty carrier.

The present density of LNG traffic is insufficient to expect a arrier to be available within a short period. For example, at a U.S. eceiving port which is geared for one ship arrival every 10 days, if n outbound ship has a casualty within 24 hours of its expected in-port rrival time; the next scheduled ship can advance its ETA by two days ue to the emergency; and, if the next ship required one day for unoading and one day to approach the transfer, the waiting period of the amaged ship is 11 days (1 + 10 - 2 + 1 +1 = 11). Diversion of an mpty ship from another port might abbreviate such a waiting period. hen terminals such as Lake Charles, Elba Island, Everett, and Cove oint are all in full or expanded operation, such inter-port cooperatior ay be feasible.

The provision of stand-by ships at the various ports for this urpose is feasible, but cannot be justified economically; the sole .S. LNG barge (MASSACHUSETTS) is of small capacity and moreover is ot in commission.

fully manned and operable and must be cooled down to be of use
expense of the LNG ships prohibits, under current economics in
even a laid-up ship costs on the order of $90,000 per day and
ing ship well over $100,000 per day, the stand-by of an opera
ship in unemployed manner for contingency use could cost over
million per year, per ship.

A storage barge would be somewhat less expensive for sta
but could still represent a large investment since the cargo
is the largest portion of the vessel's cost. General Dynamic
offers its 25,000-M^3 spheres for a price in the $6 million r
A seaworthy 125,000-M^3 barge would cost well over half the co
equivalent ship, since the cargo system, including all safety
strumentation features, would be similar to those of an equiv
sized ship.

Another option would be to provide a 25,000-M^3 barge suf
to offload one tank at a time. This would extend the total o
time and thus might not be practical, but it would be appreci
less costly. Such a barge could be fitted with any number of
tank systems. The barge, MASSACHUSETTS, with four horizontal
drical tanks, has a capacity of only 4,700 M^3 (30,000 bbl).

Ship-to-ship transfer also requires flexible or articula
fer lines that would be difficult to design so they could be
used and would stand up under the unusual dynamic loads to wh
they might be subjected.

6.5.5.4 Disposal of LNG with Equipment External to the

The use of equipment to flare or otherwise burn the LNG
under controlled conditions at sufficient distance from the I
offers the advantage of not having to equip every ship with t
essary systems. This would reduce the amount of retrofit rec
and eliminate the need to sacrifice cargo space for the dispo

ote from the tanker include the following:

- Burning LNG on the Water Surface

  Perhaps the simplest concept is to pipe the liquid a safe distance from the tanker, discharge it onto the water surface, and ignite it. This might require long flexible lines to keep the flame at a safe distance from the tanker. There might be areas where it would not be possible to find a safe location for the pool fire where the thermal radiation would not cause damage to built-up areas near the shipping channel. Nevertheless, the simplicity of the system warrants further evaluation.

- Submerged Combustion

  Some vaporizers employed at LNG plants burn natural gas and air under water; the heated water is then employed in a heat exchanger arrangement to warm up or gasify the liquid. A similar system might be devised to dispose of the LNG at a distance from the tanker. This concept, however, would require a barge-mounted vaporizer system and large blowers to force air into the water, along with the natural gas, for combustion purposes. This system would appear to be inordinately expensive because of the large blowers needed to achieve sufficient pressure differential to force the gases well below water level. It does, however, eliminate thermal radiation hazards from open flames.

- Gas Turbine Combustors

  In this concept a bank of jet engines would be used to convert the energy of combustion to mechanical energy which might then be dissipated by one of several different means, including some form of thermal dissipation in the water. The cost of such a system, however, would appear to be excessive compared to other potential concepts. Gas turbines basically contain a level of sophistication far above that deemed necessary for merely disposing of the heat of combustion.

for a single engine to absorb the contents of one 25,000-M^3

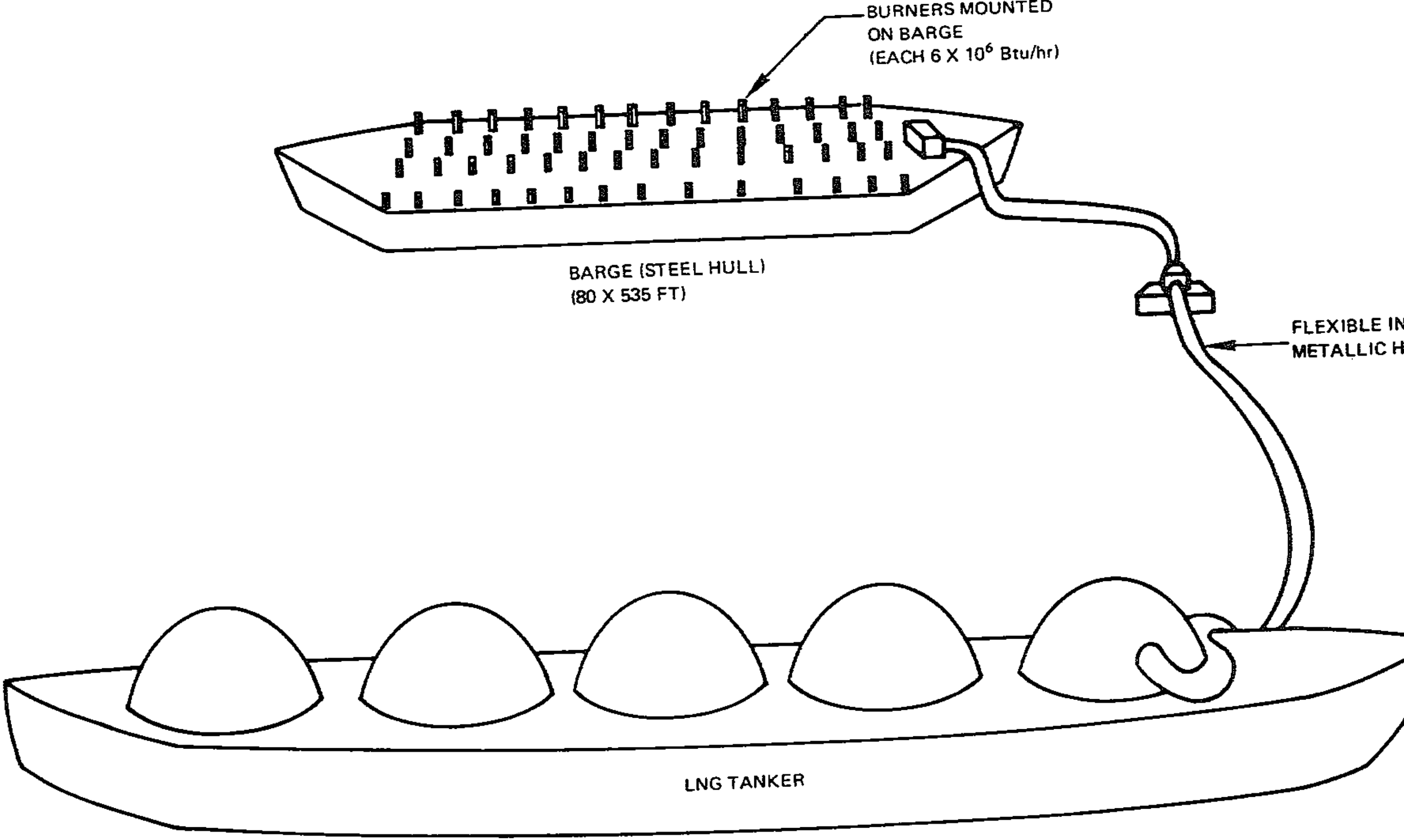
- Waste Heat Boilers

  Waste heat boilers are much less expensive than gas turbine and could conceivably provide for the disposal of the LNG c within a day or two. It is estimated that with 10 boilers a barge and 4 barges, a high rate of disposal could be achi Each boiler of conventional design capable of 500 x 10^6 Btu would be expected to cost about $200,000. A preliminary es would indicate that a waste heat boiler system might cost b $10 and $20 million.

  The problem of utilizing sea water in these boilers and dum steam overboard requires further evaluation of this concept

- Open Flares

  Barge-mounted flares would be similar to pool burning, but be controlled better and provide a means of reducing the si of the flame and, hence, the thermal radiation hazard. A c cept using a large matrix of off-the-shelf flares or burner illustrated in Figure 6.2. This one large barge would be capable of disposing of the contents of the remaining cargo the tanker within a day or two. Not shown are the vaporize necessary to convert the LNG to vapor before being transfer to the flares. Preliminary estimates indicate that the cos of this system might be in the range of $6 to $10 million.


BURNERS MOUNTED
ON BARGE
(EACH 6 X 10^6 Btu/hr)
BARGE (STEEL HULL)
(80 X 535 FT)
LNG TANKER

minary survey of cargo disposal needs and methods are as

6.6.1 Conclusions

- It is unlikely, but possible, that an LNG tanker grounded, disabled, and/or damaged to the extent loading of LNG at other than receiving terminals preferred response to the accident.
- Emergency off-loading times of less than a day to depending upon the condition of the tanker, may b to adequately remove a perceived threat to the su
- It is unlikely that the cargo could be off-loaded within these periods of time (at other than the t with existing equipment and plans, short of scutt
- The most desirable method of off-loading cargo is it to another vessel(s) since this would allow th cargo to be salvaged. But because of the availab existing and planned vessels that could receive t only rarely would the conditions be right for tra the interval of time that is required for removal perceived or real threat.
- Shipboard methods of disposing of cargo (e.g., by or utilizing specially designed combustors) appea too hazardous or require equipment that may call inordinate amount of space on the ship.
- The transfer of cargo through flexible lines to a located at a reasonable stand-off from the ship v the means to dispose it of by a matrix of flares of waste heat boilers. This system appears to be

and safe for use in relatively sheltered waterways, but might present severe problems when and where sea states may be high.

A compromise, or perhaps an interim measure, that needs more evaluation is the pool burning of cargo by releasing and burning it on the water at a sufficient stand-off from the ship and vulnerable surroundings. Again flexible transfer lines would be used to carry the LNG ship to the site of pool burnings.

.4.2 Recommendations

Criteria for equipment and methods needed to dispose of or salvage LNG cargo from a damaged or disabled tanker should be defined more accurately.

Depending upon the risks presented by LNG shipping, an analysis should be considered for each LNG project so as to:

- characterize potential failure modes and their consequences in detail as a function of possible ship location for the specific ships and for the specific waterways being traversed;
- establish risks to the surroundings from these accidents;
- determine when and under what conditions salvage or disposal may be necessary, define required offloading times; and
- establish criteria for the design and use of salvage or disposal equipment and methods.

Salvage or disposal methods should be developed and made available for use, as defined by the above criteria and needs.

As an interim measure, the development of a portable system for the pool burning of LNG at safe stand-off distances should be evaluated in detail and the necessary equipment should be developed and deployed if such an evaluation concludes that the system would be cost-effective.

Equipment should be developed and made available (where it does not now exist) for handling emergency offloadings (at LNG terminals) from damaged or failed LNG tankers.

All U.S. import projects have been subjected to ex
evaluations. Primary focus on shipping accidents has b
ship collisions for they appear to be the most likely m
large spill could occur, even though the likelihood of
ing is extremely small. Little has been done, however
outline the response that should be taken once a severe
occurred. At least in the open literature, there is li
commentary on what to do with a damaged (fully or parti
ship in an emergency.

Without having identified all of the credible even
and planning ahead-of-time for response to them presen
inadequate response will cause unacceptable casualties
that resulting from the early phases of the accident or
addition, indecision, vacillation, and delay that may
result of the lack of detailed and appropriate conting
may cause undue alarm, forcing imprudent responses, ac
excessive expenditures of labor and money, and unfound
on further shipping of LNG. It appears that it would
develop or improve upon contingency plans for respondi
dents even though their occurrence is expected to be r
never happen.

In this study we have outlined the items that may
development or improvement of contingency plans that r
disposal of the cargo. The content of such plans, of
and when more definite salvage and disposal measures a

6.7.2 Components of a Contingency Plan

The components of contingency plans described her
preliminary assessment of conditions that may possibly
or disposal of cargo from the LNG tanker. The followi

developed in the future.

6.7.2.1 Plans for Damage Assessment

Once an accident has taken place and events begin to evolve, the sessment of the condition of the ship and its cargo system becomes itical to the implementation of adequate response. Plans need to be veloped that would allow appropriate assessment to be made, taking to account possible crew incapacitation, lack of normal communications th the ship, inability to board the vessel, and other restrictions troduced by the accident and its consequences.

Of particular importance is the monitoring of the onboard cryogenic stem. This includes the integrity of the insulation and the LNG ntainment and its structural support as well as the condition of ansfer lines, valves and the cryogenic control system. Tank pressure ild-up, adequacy of relief, and pending venting of vapors or tank ilure are also, of course, critical to implementing pertinent and imely response actions.

The ability to assess the condition of the ship itself will also lay a significant role in the response decision process. Flooding, eaworthiness, risk of further damage, ship motion, grounding, listing nd other factors must be considered and evaluated.

Plans should be made for appropriate engineering drawings, operaing procedures, and personnel with the necessary skills to be made ccessible so that the condition of the ship may be assessed as events ccur following the accident.

Plans should also contain basic responses that may be necessary, epending upon the possible outcomes of damage assessment.

.7.2.2. Plans for Response Action

There are generally two somewhat distinct response phases that pply to hazardous chemical shipping accidents, as described and mployed in the development of the Chemical Hazards Response Information

there is time to make a more complete assessment of the condition of the ship and its contents and before longer term responses can be initiated. In this first phase, fire fighting, rescue, and protecti of surrounding areas and activities will be carried out. In additio acquiring information for damage assessment and the reporting on the course of events to those that are trained to evaluate them must be performed.

Detailed plans, based on assessments of the potential accidents and subsequent events, for the initial or first-phase responses shou be developed for specific import projects where they do not now exis

The second phase of response actions consists of preparing for a implementing damage assessment procedures, providing manpower and equipment, assigning responsibilities, making appropriate response decisions, and carrying out the necessary active measures as needed. It is this second phase where much additional planning could help to ensure appropriate responses that may result in the saving of lives, reduction in losses to property, and a general mitigation of concer as to the overall response.

6.7.2.3 Planning, Responsibilities, and Incentives

The U.S. Coast Guard is in control of LNG ship movements in U.S. waters and regulations are issued under the authority of the local Captain of the Port. In the event of a casualty to an LNG carrier, t Coast Gurad representative remains as On-Scene Commander (OSC), who draw upon Coast Guard, commercial, or governmental resources. Under current procedures, the Coast Guard has one or more patrol boats or cutters present at each ship movement, and is in charge of the commu cation network which links together the entire operation. In the event of a casualty, the immediate need may be for fireboats and tug

As OSC, the Coast Guard will be responsible for approving or dis approving further methods of cargo disposal in the light of the risk

instituting any shoreside alerts or evacuations.

If the ship is damaged or disabled, but the cargo system remains intact, the responsibility for determining repair and salvage measure rests with the ship's owners, subject only to approval or disapproval of the Coast Guard in respect to the interference such measures may cause to the operation of the port. In such an instance, it is highl probable that a decision will also have to be reached concerning disposition of cargo or extended boil-off.

If ship-to-ship cargo transfer is possible, the nearest terminal will be the organization best qualified to determine availability of ships and to arrange for this use. If the LNG carrier which has been damaged is in a "safe" condition, the terminal must be brought into the planning for cargo unloading to shore immediately, if the ship ca be moved to the terminal.

Other than tugs or fireboats, there is little material or equipme which is of use in the event of an LNG ship casualty, other than the actual ship repair or spare parts which may be needed if sufficient t place the ship in operation again. The OSC would be the contact poin for all other agencies and organizations which might be involved in the effects or potential effects of an LNG ship casualty.

Present Captain of the Port plans for LNG ship movement and the ship's own emergency plans cover much of the above. However, it appears that more attention to the detailed actions (based on real accident scenarios) that may be taken after a major failure should be considered. If salvage or disposal methods are developed, then the contingency plans would have to be expanded to provide technical information on these systems and to provide policy and guidelines for their implementation.

CRITERION FOR CLASSIFYING SPILLS INTO INSTANTANEOUS AND CONTINUOUS TYPES

The maximum radius of spread for an instantaneous released LNG spill given by[1]:

$$R = \left[\frac{V^3 g\Delta}{\dot{y}^2}\right]^{1/8} \tag{A1}$$

The maximum spread radius for a continuous spill is:

$$R = \left[\frac{V}{t_s} \quad \frac{1}{\pi \dot{y}}\right]^{1/2} \tag{A2}$$

The above two equations can be written in dimensionless form by defin certain characteristic parameters. These are:

$$\left.\begin{aligned} L &= \text{characteristic length scale} = V^{1/3} \\ t_{ch} &= \text{characteristic evaporation time} = \frac{L}{\dot{y}} \\ \xi &= \text{dimensionless maximum spread} = \frac{R}{L} \\ \tau &= \text{dimensionless time} = \frac{t}{t_{ch}} \end{aligned}\right\} \tag{A3}$$

Using the above parameters equations A1 and A2 are written as:

$$\xi = \left[\frac{Lg\Delta}{\dot{y}^2}\right]^{1/8} \quad \text{INSTANTANEOUS} \tag{A4}$$

$$\xi = \frac{1}{\sqrt{\pi}} \quad \frac{1}{\tau^{1/2}} \quad \text{CONTINUOUS} \tag{A5}$$

The above two equations are shown plotted in Figure A.1. It is seen the dimensionless radius for instantaneous spill is somewhat insensit to the spill volume in the range of 1000 m^3 to 25,000 m^3. In the cas of continuous spill, the radius of spread is inversely proportional t the square root of the spill time.

It is seen from the figure that for any spill time larger than about in dimensionless units, the spill can be considered to be essentially tinuous. That is:

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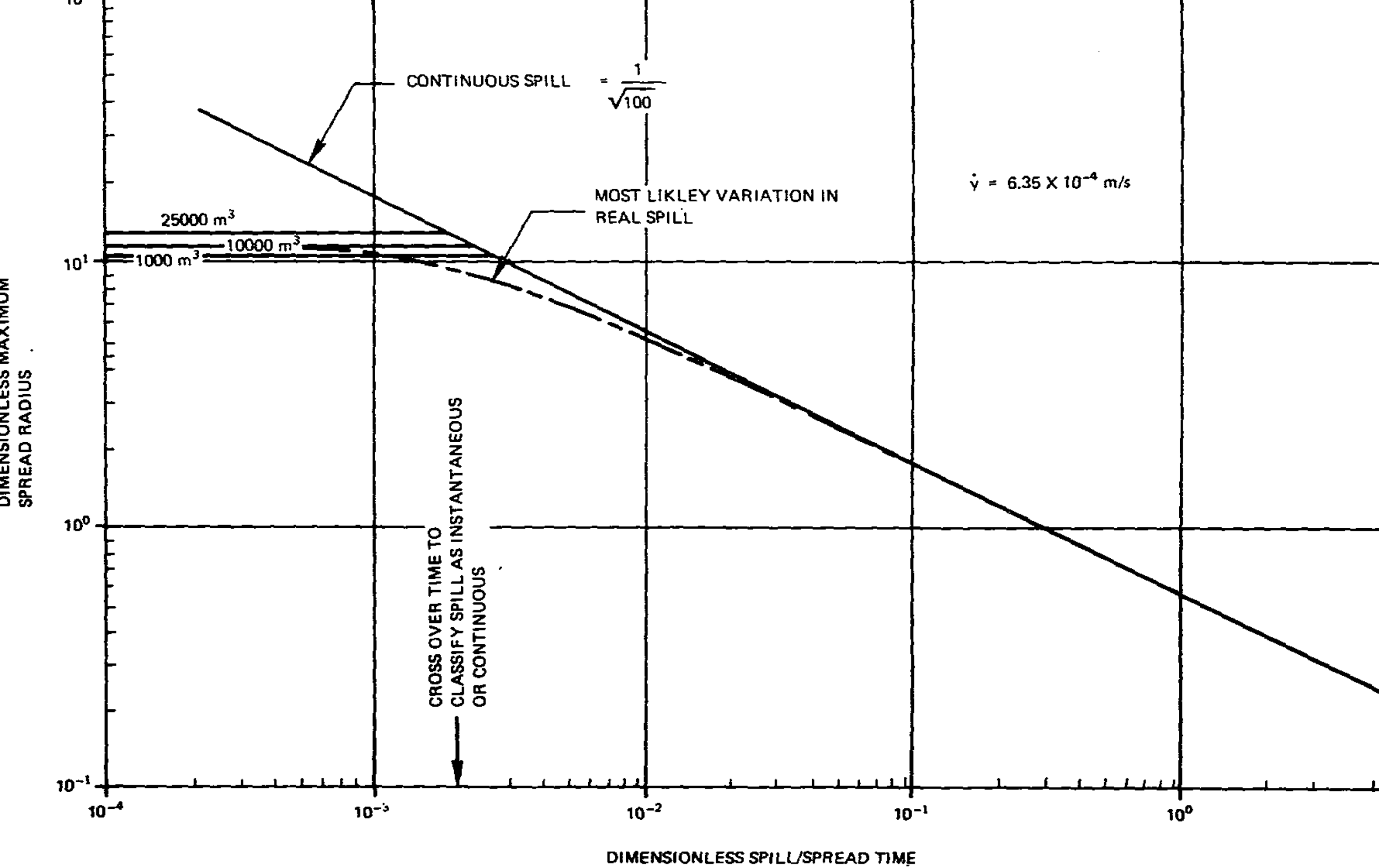
(1) See Reference 1, page 4-3.



CONTINUOUS SPILL $= \frac{1}{\sqrt{100}}$
MOST LIKLEY VARIATION IN REAL SPILL
$\dot{y}$ = 6.35 X 10^{-4} m/s
25000 m^3
10000 m^3
1000 m^3
CROSS OVER TIME TO CLASSIFY SPILL AS INSTANTANEOUS OR CONTINUOUS
DIMENSIONLESS MAXIMUM SPREAD RADIUS
DIMENSIONLESS SPILL/SPREAD TIME
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}

below.

EXAMPLE:

25,000 m^3 of LNG is spilled over a period of 3 minutes. Is this sp be treated as a continuous spill or an instantaneous spill? Assume spill is on fire and that the liquid vaporization rate is 6.35 x 1((1.5 inch/min).

$$\text{Characteristic length} = L = (25{,}000)^{1/3} = 29.2 \text{ m}$$

$$\text{Characteristic evaporation time} = t_{ch} = \frac{L}{\dot{y}} = \frac{29.2}{6.35 \times 10^{-4}} = 4604$$

Hence, crossover time $t_{crossover} = \tau_{crossover}\ t_{ch} = 0.002 \times 46047 =$

Since the spill duration is 180 s and is longer than the crossover of 92 s, the spill can be treated as a continuous spill. Had the s occurred in 1 minute, then it should be modeled as an instantaneous

APPENDIX B

A MODEL FOR THE GRAVITY SPREAD OF A HEAVY VAPOR RELEASED CONTINUOUSLY FROM A SOURCE

Appendix a model is derived to determine the rate of spread of a than air vapor when it is released continuously. The key concept used is the dilution of vapor by air entrainment during the lat- ead. Expressions are derived for the width of cloud and the mean ation of vapor in the cloud.

of initial density ρ_v is released at a volumetric rate of $2\dot{V}$ from of semi-width y_o. The wind speed is U_w. Determine the spread the vapor.

ONS

ing the model we assume the following:

air in the ambient is dry;

the spread of vapor is only in the lateral (crosswind direction);

a parcel of vapor released moves downwind at wind speed;

entrainment of air is effected only by the lateral spread speed of the vapor;

the vapor cloud has uniform concentration and height at any given instant of time;

air and the vapor are perfect gases with the same molar specific heats;

the mixing of air and vapor is adiabatic.

-1 shows schematically the essentials of the model. The rectangular ction of the vapor cloud expands due to air entrainment and moves d at wind speed.

UATIONS

der a slice of the cloud of unit distance in the windward direction ion x (see Figure B-1b). The equations of mass conservation, volume tion, spread law, and the entrainment equation are written as follows ed.*

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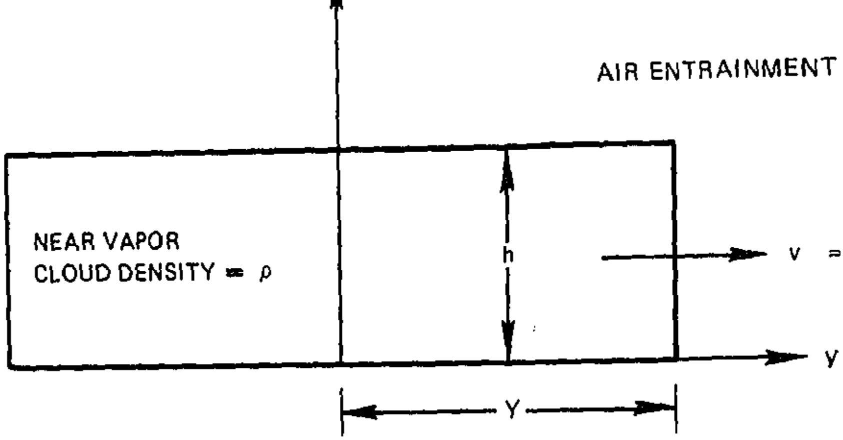
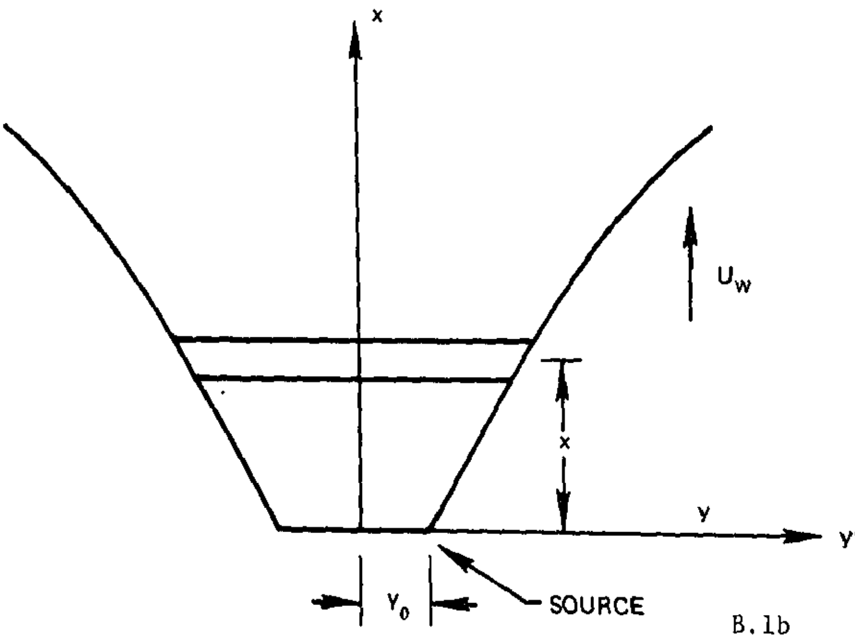
ls are described in the nomenclature.



B.1a



B.1b

FIGURE B.1 SCHEMATIC REPRESENTATION OF THE LATERAL SPREAD MODEL

(i) Entrainment Law

$$\underbrace{\dot{m}'}_{\substack{\text{Rate of mass}\\ \text{entrainment on}\\ \text{one side of}\\ \text{cloud at the top}}} = \left(\frac{1}{2}\right)\beta\, \rho_a\, yv \tag{B1}$$

The 1/2 on the right-hand side accounts for the fact that only the edge moving laterally at velocity v.

(ii) Spread Law

$$v = \frac{dy}{dt} = \sqrt{2gh\left(\frac{\rho}{\rho_a} - 1\right)} \tag{B2}$$

where ρ is the mean density of the vapor cloud.

(iii) Volume Conservation Law

If A is the cross sectional area (to one side of the centerline) of the cloud, then we can write:

$$A = A_o + A_a \tag{B3}$$

where A_a is the total volume of air (per unit length in wind direction) entrained on one side of the vapor cloud. The above linear addition of v can be made because, in the adiabatic mixing of perfect gases having the molar specific heat, the total volume of the mixture is equal to the su the individual vapor volumes.

$$A_a = \frac{1}{\rho_a} \int_o^t \dot{m}'\, dt = \frac{1}{\rho_a} \left[m' - m_o'\right] \tag{B4}$$

(iv) Mass Conservation

The total mass of gases in the slice of cloud is equal to the initial m together with the entrained air mass. That is:

$$m' = m_o' + \int_o^t \dot{m}'\, dt \tag{B5}$$

$$m' - m'_o = \frac{1}{2} \; \frac{\beta \rho_a}{2} \; (y^2 - y_o^2) = \rho_a A_a$$

Hence:

$$A_a = \frac{\beta}{4} \; (y^2 - y_o^2)$$

Now:

$$\rho = \frac{\text{mass}}{\text{volume}} = \frac{m'}{A} = \frac{m'_o + \rho_a A_a}{A_o + A_a}$$

Hence:

$$(\frac{\rho}{\rho_a} - 1) = \frac{m_o - \rho_a A_o}{\rho_a A}$$

Also:

$$A = yh$$

Substituting B8 and B9 in equation B2 we get:

$$\frac{dy}{dt} = \sqrt{2gh \, \frac{\left(m'_o - \rho_a A_o\right)}{\rho_a yh}}$$

Integrating we get:

$$\frac{2}{3} \left(y^{3/2} - y_o{}^{3/2}\right) = \sqrt{2g \, \frac{\left(m'_o - \rho_a A_o\right)}{\rho_a}}$$

i.e.

$$\left(y^{3/2} - y_o{}^{3/2}\right) = \frac{3}{2} \sqrt{2gA_o\left(\frac{\rho_v}{\rho_a} - 1\right)} \quad t$$

$$\left\{ \left(\frac{y}{y_o}\right)^{3/2} - 1 \right\} = \frac{3}{2} \sqrt{2gh_o\left(\frac{\rho_v}{\rho_a} - 1\right)} \quad \frac{x}{U_w}$$

This gives the spread law with distance. We now define the follow characteristic parameters:

$$= \frac{y_o}{\sqrt{2gh_o\left(\frac{\rho_v}{\rho_a} - 1\right)}} = \frac{y_o}{v_o} = \text{characteristic spread time} \qquad \text{(B14)}$$

$$= \frac{t}{t_{ch}} = \frac{x}{U_w t_{ch}} \quad \text{dimensionless time}$$

uation B13a becomes:

$$= 1 + \frac{3}{2}\tau \qquad \text{(B13b)}$$

ctional area of slice (from equations B6b and B14a) is given by:

$$\Lambda_o + \frac{\beta}{4} y_o^2 [\xi^2 - 1] \qquad \text{(B15)}$$

ncentration of vapor:

$$\text{ass} = \frac{\text{mass of vapor in the slice}}{\text{total mass of vapor/air mixture}} = \frac{\rho_v \Lambda_o}{m'}$$

$$\text{ass} = \frac{\rho_v \Lambda_o}{\rho_v \Lambda_o + \rho_a \Lambda_a} = \frac{1}{\left[1 + \frac{\rho_a}{\rho_v}\ \frac{\beta}{4}\ \frac{y_o^2}{A_o}\ (\xi^2 - 1)\right]} \qquad \text{(B16)}$$

ly the mole concentration is given by:

$$\text{ole} = \frac{1}{\left[1 + \frac{\rho_a}{\rho_v}\ \frac{\mu_v}{\mu_a}\ \frac{\beta}{4}\ \frac{y_o^2}{\Lambda_o}\ (\xi^2 - 1)\right]} \qquad \text{(B17)}$$

d velocity of spread (from equation B10)

$$= \sqrt{2g\ \frac{\Lambda_o}{y}\left(\frac{\rho_v}{\rho_a} - 1\right)} = v_o\sqrt{\frac{y_o}{y}} = \frac{v_o}{\sqrt{\xi}} \qquad \text{(B18)}$$

TERMINATION OF LATERAL GRAVITY SPREAD

The lateral spread of vapor induced by gravity becomes small whe mixing on the edges is dominated by atmospheric turbulence. The simple criterion by which such a termination of gravity spread c measured. Therefore, we have assumed a very simple gravity spre criterion. The lateral gravity spread is assumed to terminate w combined vector velocity due to wind and lateral gravity is less times the wind speed. This translates into a terminating gravit velocity of 50% of wind speed.

SPECIFIC EXAMPLE

Consider the spill of 25,000 m^3 of LNG onto water surface in a d minutes. It is desired to describe the gravity spread of the va ated by the LNG boiling on water. Following specific parameter used:

Quantity of LNG spilled	=	25,000 m^3
Density of LNG	=	425 kg/m^3
Density of LNG vapor	=	1.84 kg/m^3
Regression rate on water	=	4.23×10^{-4} m/s
Density of air at ambient condition	=	1.2 kg/m^3
Wind speed U_w	=	3 m/s
Entrainment coefficient β	=	0.1

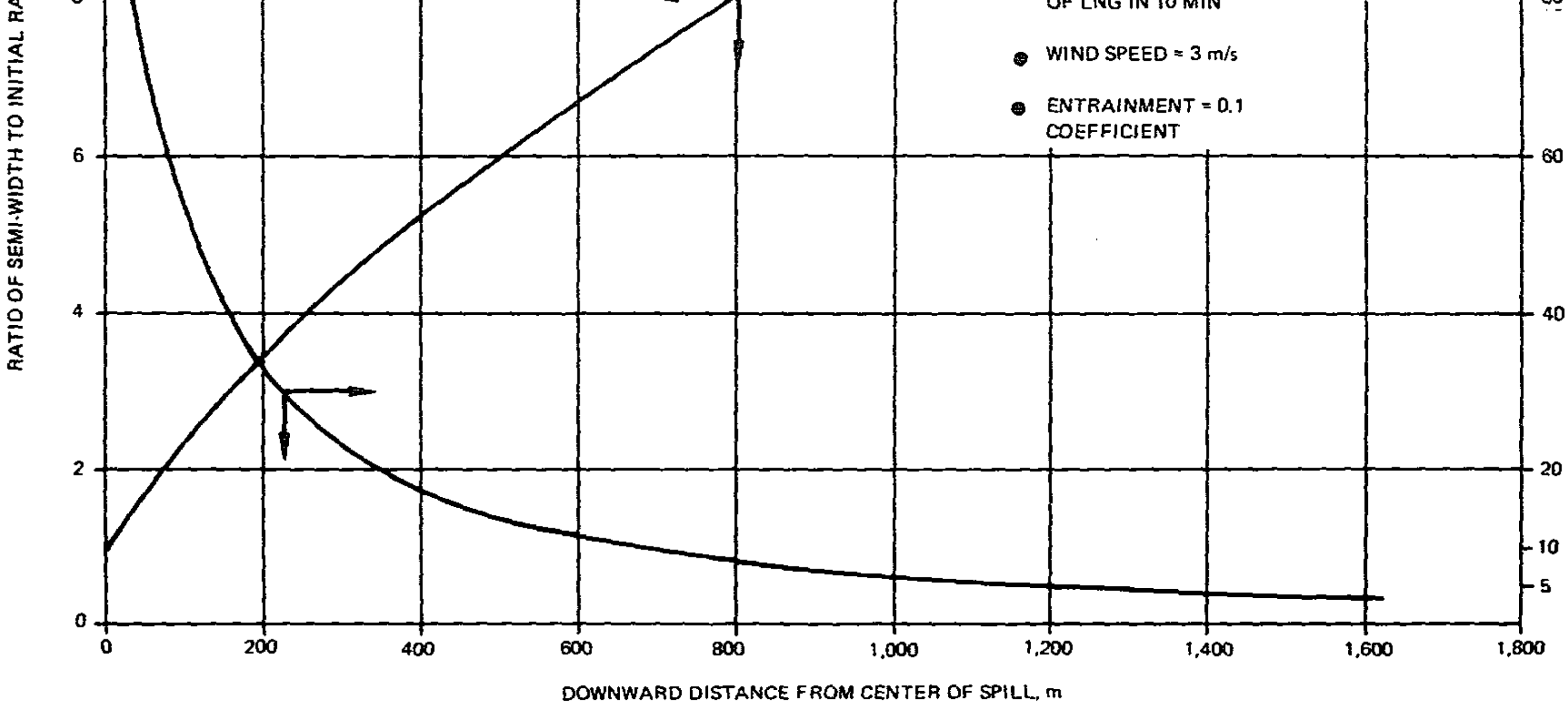
Hence,

Maximum radius of spread = R	=	177 m
Volumetric flow rate of vapor in one half of the center line = $\dot{V}$	=	4812 m^3/s
Initial thickness of vapor cloud = h_o	=	$\frac{\dot{V}}{R\,U_w} = 9.06$ m
Initial lateral spread velocity = v_o	=	9.73 m/s
Characteristic time = t_{ch}	=	18.19 s

The half width of spread and the mean vapor concentration (mole plotted as functions of downwind distance in Figure B.2 for the a

RESULTS

It is seen that within a distance of about 1 km downwind the mea centration is reduced below flammable limit. The semi-width of this stage is about 10 times the initial semi-width; that is the is about 1800 m.



LATERAL GRAVITY SPREAD OF
LNG VAPOR FROM A CONTINUOUS
SPILL OF LNG ONTO WATER

FIGURE B.2 LATERAL GRAVITY SPREAD OF LNG VAPOR FROM A CONTINUOUS SPILL OF LNG ONTO WATER

A_a	=	total volume of ambient air entrained per unit windward length of cloud	m^2
A_o	=	initial cross sectional area of cloud	m^2
C	=	concentration of vapor in the cloud	
g	=	acceleration due to gravity	m/s^2
h	=	height of cloud	m
m'	=	mass of vapor in a slice of cloud of unit length in the wind direction	kg/m
t	=	time	s
U_w	=	wind speed	m/s
v	=	lateral spread speed of cloud	m/s
x	=	downwind distance	m
y	=	crosswind extent of cloud	m

GREEK

β	=	entrainment coefficient	
μ	=	molecular weight of species (air, vapor, mixture)	kg/k
ξ	=	dimensionless lateral spread	
ρ	=	density	kg/m^3
τ	=	dimensionless time	

REPORT H

Safety Assessment of Gelled LNG

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TABLE OF CONTENTS

FIGURES

SUMMARY

The objective of the program is to characterize the gelled LNG for
cess, flow, and use properties and to demonstrate the degree of safety
ancement which can be achieved by gelation. To attain the objective, a
e-task technical program is planned. The tasks are:

Task 1 - Gel Preparation

Task 2 - Gel Characterization

Task 3 - Safety Evaluation Tests

Task 4 - Preliminary Design of Industrial-Scale Gelation System

Task 5 - Preliminary Economic Assessment

This paper presents a brief discussion of the development of gelle
a discussion of the state-of-the-art, a discussion of the potential
fits to be attained from gelation, a program plan, and documents the
ress to date on the program.

INTRODUCTION

The projected importation of large quantities of LNG into the U. a result of the domestic natural gas shortage, has generated considera blic concern and resistance, because of the potential danger of catastr plosion or asphixiation from vapor clouds formed by the rapid evaporati cidentally spilled LNG. Projections of LNG imports of about 5 billion 1980 and over 10 billion cfpd by 1990 indicate that by 1990, ships wi f-loading at the rate of five ships per day with about 15 LNG carriers S. ports at all times. Therefore, the potential for accidental spill r lting from collision, etc., cannot be considered negligible, and the nsequences of a major spill, especially in a populated and/or industria ea, are totally unacceptable.

The characteristic of LNG which causes the problem is the rapid s the spilled liquid over the surface, creating a very large heat transf ea and, hence, a very rapid evaporation. Preventing the rapid spread o ill would reduce the overall evaporation rate to a level where natural rsion could keep cloud concentrations to an acceptable level. If, in dition, a means is found to reduce the evaporation rate per unit surfac ea of the spilled LNG, this will reduce the overall evaporation rate e rther, and would be of great benefit.

A promising method of preventing the rapid spread of spilled LNG ducing its vaporization per unit surface area is to convert the liquid semi-solid (viscoelastic) state by gelation of the liquid. This can be complished by thoroughly dispersing 2-4% of water in vapor form in the form the gel. Methanol can also be used as gelant, but significantly eater concentration levels are required to produce gel structure compar that produced by using water as the gelant.

The objective of the current program is to demonstrate on a small sis the degree of safety enhancement that can be attained by use of gel

versus ungelled LNG. In order to achieve the objective, the gels used tests should be well characterized and the test conditions should simul common handling practices as closely as is practical on a small scale.

Since 1962, Aerojet has been actively engaged in the gelation o cryogenic liquids for use in rocket and jet engines. The liquids which been gelled are nitrogen, oxygen, hydrogen, oxygen difluoride, diborane methane. The initial gelants used were commercially available, finely d particulates such as pyrogenic silicas and colloidal carbon materials. ever, excessive quantities of these materials were required and signifi fuel value degradation occurred because of this. In 1967, a method was developed by which ultra-fine particles of energetic materials could be pared in situ with the cryogenic liquids.

STATE-OF-THE-ART

Following that development, the cryogenic propellants could be without significant performance degradation. The ability to gel methan particles prepared from water, methanol, trimethylaminoborane, and tri-methylaminoboron trifluoride led to the award of a contract by the NASA Aerojet in 1970 for the "Investigation of the Suitability of Gelled Met for Use in a Jet Engine", with the SST being the vehicle of considerati The program resulted in the development of methane gels which could pre the solubilization of nitrogen in the gelled methane with gelant concen as low as one weight percent in the liquid methane and the gelled produ successfully flowed through a heat exchanger which simulated the transf required for a jet engine.

Under the NASA contract, limited, small-scale tests were conduc involving the boil-off behavior of the gelled methane, the expulsion ef

ttainable with the gels, and the storability of the gels. The results favorable, but no extensive characterization of the gel properties was onducted except for the inhibition of gas dissolution in the gel. The rogram plan was to extend the work to LNG under a follow-on contract; u ortunately, the SST was cancelled at this time and required funding was onger available.

Subsequently, additional work was conducted at Aerojet under IR& rder to develop a continuous process for the gelation of LNG.

The gelation of liquid methane and LNG also has been investigate sing the ALRC gel preparation methods at the Massachusetts Institute of echnology under the American Gas Association sponsorship by Dr. Robert eid and Lucile M. Shanes. The investigation was motivated by the poten safety enhancement which gels afford in comparison to the neat liquids. nvestigation itself was directed towards a fundamental understanding of elants and the gel characteristics and led to the publication of a doct hesis by L. M. Shanes[2].

Data in the thesis demonstrates reduced boil-off rates of LNG elled with methanol from water surfaces as compared to ungelled LNG and here is discussion of the safety enhancement that can be achieved by ge sing limited data in various models. The tests were conducted generall pint or less of the gelled material.

Prior to this program the knowledge of the gelled methane and ge NG was restricted to:

Viscosity data at very low shear rates, much lower than encounte in normal transfer and handling.

Some yield stress values as a function of gelant concentration.

Approximate composition of the gelant particle itself.

A demonstration of gel conversion to gaseous methane in high flux system, 5000 to 20,000 Btu/hr-ft^2.

Reduced boil-off rates from water and glass surfaces as comp the neat liquids.

The gel's ability to inhibit gas dissolution in the gelled l

The expulsion of gels from small containers.

No significant gel structure degradation during four-five da storage.

The degrease of spillage rates of gel as compared to the nea

In order to utilize the gels on a larger scale, the followi required:

Flow characterization of gels over a range of shear rates (sec^{-1}) that are normally encountered in transfer and handli

Definition of the optimum gelant and gelant concentration r to enhance the safety characteristics of LNG.

Determination of the aging characteristics of the gels over of a month.

Flow characterization of the gels under low heat flux condi

Stratification evaluation of the gels under storage and low flux conditions, 10-100 Btu/hr-ft^2.

Large-scale tests of gel spillage and boil-off rates for co to the LNG itself.

All the above information can be acquired concurrent and pr development of an industrial-scale process for preparation of the g fact, unless all the above are favorable for the usage of the gels, ment of an industrial-scale process is not warranted.

The benefits associated with gelled LNG may be divided into tw categories that are interrelated:

- Increased Safety
- Reduced Boil-off

Assessment of the benefit of gelled LNG comes down to estimati maximum distance at which a flammable gas mixture can result after a m spill. This requires a detailed model of the spill including knowledg the type of spill, i.e., instantaeous or continuous, how fast it sprea the corresponding rate of heat transfer and vaporization per unit of c area. Also required is a model of the vapor cloud formation and dispe with time. The maximum distance reached by a flammable gas is directl related to the maximum rate of vapor generation and this, in turn, is estimated using the maximum pool diameter and an appropriate average b rate. Thus, the maximum pool diameter and boil-off rate are the two m important parameters that determine the extent of the flammable plume. size, however, is dependent on the spreading rate of LNG. On the basi an assumed steady-state yield stress of 500 dynes/cm^2 for gelled LNG, resulting in a (calculated) spreading rate of approximately one-third of LNG, it has been estimated[2] that the maximum flammable distance c reduced by a factor of five. According to current practice, the dange extends five miles from a storage site. Current plans for the Pt. Con California site, according to the Public Utilities Commission, is to c the danger zone to extend 4.5 miles. By reducing this distance to one 75 square miles become safe and available for normal use. Such gains a substantial economic advantage for gelled LNG, but must be verified mentally by means of large spill tests.

Safety is not an easily measurable quantity, but considering t potential for large-scale damage is so great, the large reduction in t area must represent a vast improvement in safety.

LNG boil-off is an unavoidable phenomenon that takes place from time natural gas is liquefied to the time it is regasified. The amount boil-off depends on the length of time the LNG is in liquid form and the degree of insulation that is provided for its storage, transport, and lo and unloading operations. For example, on a typical seven-day trip (336 miles), the following gas losses are sustained:

Loss During Loading Operation	1.00%
Boil-off During Voyage	1.75%
Loss During Unloading	0.50%
LNG Heat Retain for Return Voyage	3.00%
Total Loss	6.25%

Boil-off rates for gelled LNG have been obtained from confined s tests[2], and were found to be one-half to one-third that of LNG. Wheth these rates prevail in containment vessels such as tanks and flowing pip is not known. One can only speculate, and assume that an enclosed gel w offer a greater resistance to heat flow through the walls of its contain by virtue of a gas film that is established and held in place by the cla structure soon after the initial vaporization at the wall takes place. gelation may offer the added benefit of reduced vaporization that may re a measurable economic advantage.

Gelled LNG will eliminate tank sloshing, such as may be experien on the high seas; thus reducing not only the convective heat transfer at walls but also the dynamic loads on the tanks.

PROGRAM PLAN

To attain the objective of the program which is to characterize the
-NG for process, flow, and use properties and to demonstrate the degre
ty enhancement that is achieved by gelation, a five-task technical
is planned. The tasks are:

Task 1 - Gel Preparation
Task 2 - Gel Characterization
Task 3 - Safety Evaluation Tests
Task 4 - Preliminary Design of Industrial-Scale Gelation System
Task 5 - Preliminary Economic Assessment

a) Task 1 - Gel Preparation

Under this task, the gelling apparatus and ancillary equipment
ary for gel production and evaluation will be reassembled, installed, a
d-out. The process for gel production using both water and methanol as
g agents will be investigated with regard to carrier gas requirements.
l baseline gel preparations will utilize commercially pure methane and
g agent concentrations which will produce gels having yield stresses
g from about 200 to 1000 dynes/cm^2. Subsequent gel preparations will
e the use of two LNG's containing heavier hydrocarbons: (1) LNG-A,
ning nominally 93% CH_4 and 7% C_2H_6, and (2) LNG-B, containing nominally
$_4$, 10% C_2H_6, and 5% C_3H_8. Each of these LNG's will be gelled with
s quantities of water and methanol to produce gels having yield stress
bout 200 to 1000 dynes/cm^2. The gel preparations will nominally be of
two liters in volume and will, in general, be utilized in the Task 2 -
aracterization studies. Each batch of gel will be analyzed to determin
g agent concentration. Large (~5 gal) batches of a selected LNG gel wi
pared later in the program for use in Task 3 - Safety Tests. The gel
ition selected for these larger preparations will be based on the Task
aracterization studies.

b) Task 2 - Gel Characterization

Under this task, gels prepared under Task 1 will be char in regard to six properties or types of behavior: (1) yield stress, logical characteristics, (3) flow characteristics under simulated tra conditions, (4) expulsion behavior, (5) gel aging characteristics, an off rates under simulated storage conditions.

1) Task 2.1 - Yield Stress

Yield stress measurements will be made using the we sphere-method on each batch of gel produced under Task 1.

2) Task 2.2 - Rheological Characteristics

The rheological characteristics of selected gels wi determined under isothermal conditions (~N.B.P. of CH_4) by flowing th through coiled tubes of various diameters and at various pressure dro The tube diameters and pressure drops will be selected to simulate as possible the shear stresses and shear rates expected in industrial-sc operations. Tests will also be conducted with ungelled LNG's to prov basis of comparing gel and non-gel flow characteristics. It is antic that about ten representative gel compositions will be thus character

Several representative gels (~4) having high yield will be subjected to repeated forward and reverse flow cycles (~5 com cycles) at high shear rates to determine whether or not the gels are "shear thinning". Changes in flow rates at constant pressure drops a changes in yield stress for successive flow cycles will be used to in "shear thinning" tendencies.

3) Task 2.3 - Flow Characteristics Under Simulated Transfer Conditions

Under this task, the flow characteristics of gelled and G's will be determined under comparable nonisothermal conditions ate the transfer of LNG at low heat fluxes such as exist in vacuum- well insulated lines. These tests will be conducted at modest in the nonboiling regime, and at Reynold numbers which are in the egime for the ungelled LNG. These tests will define the flow rate ersus ungelled LNG at similar heat fluxes and pressure drops. The t flux levels will be defined from measurements of fluid temperature flow rate, wall temperature measurements, and such heat transfer may be required. It is anticipated that tests will be conducted elled LNG and with the same LNG gelled with water and methanol to ld stress values.

4) Task 2.4 - Expulsion Behavior

Tests will be conducted under slightly subcooled isothermal with methane/water gels and methane/methanol gels. In these tests, agent concentration is varied and the expulsion efficiencies and lities are defined as functions of gelling agent concentration (and s when within the measurable range). The expulsion efficiency is determining the volumetric fraction of the gel that can be trans- one standard vessel to another under a given set of pressurization The relative flowabilities of the gels are defined from efflux olumes under the given set of pressurization conditions and by he volumetric flow rate of the gels with that of the ungelled LNG.

5) Task 2.5 - Gel Aging Characteristics

Aging tests will be conducted in representa for a period of approximately one month to determine whether significant degradation in the gel structure during static an isothermal storage conditions. Measures of aging/storability visual inspection and/or gaseous N_2 absorption rates to indic of an ungelled exudate layer. The yield stress of the gels b the storage period will also be measured to define changes in of the gels.

6) Task 2.6 - Boil-off Rates Under Simulated S

Boil-off rates of gelled and ungelled LNG w under the very low heat flux conditions simulating those in s containers. The boil-off rates will be established using foa which are open to the atmosphere only via a single small diam in the insulation. In making the tests, two storage systems possible will be initially checked side-by-side against one a equal quantities of first ungelled methane then a gelled meth their relative boil-off characteristics. One of the storage designated the reference system while the other will be the t Boil-off tests will then be conducted on gels in the test sys boil-off rate of an equal quantity of the corresponding ungel simultaneously determined in the reference storage system. B will be defined by careful mass measurements of the loaded st over an extended period of time. Boil-off rates of gels in t will be corrected to the reference storage system using the r off characteristics of the two storage systems which were det baseline checkout tests.

Task 3 - Safety Tests

Based on the data acquired under Task 2, large (~5 gal) batches ted gelled LNG will be prepared (as a part of Task 1) and subjected ypes of safety tests along with corresponding tests with ungelled three types of safety tests are directed toward defining the racteristics of gelled LNG versus LNG itself in regard to: (1) spill (2) leakage behavior, and (3) boil-off behavior.

1) Task 3.1 - Spill Behavior

Five gallon quantities of the selected LNG gel and LNG l be spilled from a single source onto land and water surfaces. ossible, the spill configuration and instrumentation will correspond a one-dimensional apparatus being built up by students of Prof. at MIT. That apparatus is designed to provide gravity spread n on a variety of cryogenics and to provide a basis for testing nalytical models. Photographic documentation will be obtained n to normal test data and environmental conditions. The motion ill be analyzed to obtain approximate average boil-off rates.

2) Task 3.2 - Leakage Behavior

The leakage rates of LNG and two LNG gels having different sses will be determined in this task. The leakage paths will circular orifice and a rectangular slit having the same hydraulic the circular orifice. The head required to initiate leakage (with and the leakage rates of a fixed head will be determined in each tests will be photographically documented.

3) Task 3.3 - Boil-Off Behavior

The approximate average boil-off rates of LNG and two elled LNG's having different yield stresses will be determined for uncon -gal spills on a water surface. The boil-off phenomena will be document hotographically and the motion pictures will be analyzed to establish th ime-weighted average spill area and the time for complete boil-off. App ate average boil-off rates will be calculated from these values. These ff data will be compared with related data obtained from the one-dimensi pill apparatus used in Task 3.1.

The spill tests will be repeated in the vicinity of a n gnition source to determine differences in the ignition behavior of spil NG and gelled LNG and the effects the subsequent burning has on spread r nd boil-off rates.

PROGRAM PROGRESS

a) Task 1 - Gel Preparation

Under this task, the existing equipment necessary to conduct he program was reassembled, installed, and checked out. The process for elant particle production using both water and methanol is being determi ith regard to the injection-gas stream composition, injection-tube orifi izing, injection tube location in the preparation vessel. The checkout re conducted with methane in order to generate the initial baseline data he LNG tests are conducted with two LNG compositions, nominally 93% CH_4, % C_2H_6 and 85% CH_4, 10% C_2H_6, 5% C_3H_8. Gels are prepared in 4 liter qua

LNG gels using both methanol and water as gelants have been sing various concentrations of gelant vapor in methane carrier gas to ma

jection gas stream. Gels using water at 60, 24, 10, and 2.5 volume t vapor in the injection gas stream were prepared, while gels with ol were produced using 9.6 and 2.5 volume percent. An attempt was made duce a gel using a 25 volume percent methanol in the injection stream; antity of methanol required for gelation was too great for practical u repared using this range of injection stream gelant concentrations were terized in order to provide data for the optimization of injection gas composition and the selection of gelant type.

b) Task 2 - Gel Characterization

LNG gels prepared during the current reporting period are de- ed under Task 1. These gels were characterized according to yield stres eological characteristics. Yield stress measurements are being made the weighted-sphere method and rheological measurements are being ned by the use of flow coils. Characteristic flow data for gels using gelant at various injection stream gelant concentrations are presented les I through V. These data are plotted in Figures 1 through 5. cteristic flow data for gels using methanol are given in Table VI and ed in Figure 6. Characteristic flow curves for a comparison between ol/LNG gels and water/LNG gels prepared using similar gelant concentra- in the injection stream is presented in Figure 7. Yield stress data ned as a function of gelant content and injection stream gelant concent for both water/LNG and methanol/LNG gels are presented in Table VII.

The following significant items can be noted from the data.

First, from the yield stress data (Table VII):

- For the water gelant type LNG gels investigated, yield stress at a given gelant content generally

increases with decreasing injection stream ge
concentration.

- Within the range of injection stream gelant co tions investigated (2.5 Vol. % to 25 Vol. % ge significantly more methanol than water is requ a given injection stream gelant concentration duce LNG gels of comparable yield stress.

Secondly, from characteristic flow data and plots (Table and Figures 1-7):

- For a fixed injection stream gelant concentra

  (1) Apparent viscosity at a given shear rate with gelant content. This is true for bo LNG and methanol/LNG gels over the gelan ranges investigated for each injection s gelant concentration.

  (2) Methanol/LNG gels require a significantl gelant content than corresponding water/ to achieve similar apparent viscosities shear rate. This is true for shear rate of the comparable injection stream gelan tions investigated (~10 Vol. % and 2.5 V

- For a given gelant content, apparent viscosit given shear rate increases with decreasing in stream gelant concentration. This holds in g LNG gels using water gelant.

TABLE I

CHARACTERISTIC FLOW DATA[1] FOR LNG GELS AT 102°K PREPARED USING 60 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas) Methane	Ethane	Wt. % Gelant	Yield Stress (dynes/cm^2)	Shear Stress[2] (dynes/cm^2)	Shear Rate (sec^{-1})	Apparent Viscosity[2] (centipoise)	A... R... N...
	5	3.2	< 270	54.4	513	10.6	
	5	3.2	< 270	76.1	1472	5.17	
	5	3.2	< 270	109	2812	3.87	
	6	3.7	< 270	76.1	282	27.0	
	6	3.7	< 270	109	522	20.8	
	6	3.7	< 270	163	2270	7.18	
	8	5.1	771	141	810	17.4	
	8	5.1	771	163	825	19.8	
	8	5.1	771	185	1640	11.3	
	8	5.1	771	218	3689	5.89	

...2A, .375 in. tubing

...r stress and apparent viscosity are based on a calculated flow coil ef... ...th of 1252 cm.

...rent Reynolds numbers are calculated using apparent viscosities.

TABLE II

CHARACTERISTIC FLOW DATA FOR LNG GELS AT 102°K PREPARED

USING 25 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas)						
Methane	Ethane	Wt. % Gelant	Yield Stress (dynes/cm^2)	Shear Stress[2] (dynes/cm^2)	Shear Rate (sec^{-1})	Apparent Viscosit (centipoi
90	10	2.6	< 270	32.6	132	24.7
90	10	2.6	< 270	54.4	265	20.5
90	10	2.6	< 270	76.1	896	8.50
90	10	2.6	< 270	109	1631	6.67
89	11	2.9	270	109	792	13.7
89	11	2.9	270	163	1701	9.59

[1]Coil 2A, .375 in. tubing

[2]Shear stress and apparent viscosity are based on a calculated flow c length of 1252 cm.

[3]Apparent Reynolds numbers are calculated using apparent viscosities.

TABLE III

CHARACTERISTIC FLOW DATA[1] FOR LNG GELS AT 102°K PREPARED USING 24 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

e LNG Gel as Gas) thane	Wt. % Gelant	Yield Stress (dynes/cm^2)[2]	Shear Stress[2] (dynes/cm^2)	Shear Rate (sec^{-1})	Apparent Viscosity[2] (centipoise)	Apparen Reynold Number[3]
7	2.2	<270	54.4	355	15.3	82.8
9	2.8	<270	54.4	133	40.9	11.8
9	2.8	<270	109	546	19.9	99.3
2	3.7	270	109	466	23.3	74.2
2	3.7	270	163	1129	14.4	290

.375 in. tubing

ess and apparent viscosity are based on a calculated flow coil length of 1252 cm.

Reynolds numbers are calculated using apparent viscosities.

TABLE IV

CHARACTERISTIC FLOW DATA[1] FOR LNG GELS AT 102°K PREPARED
USING 10 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

Approximate LNG Comp. of Gel (Volume % as Gas) Methane	Ethane	Wt. % Gelant	Yield Stress (dynes/cm^2)	Shear Stress[2] (dynes/cm^2)	Shear Rate (sec^{-1})	Apparent Viscosity (centipo
95	5	1.2	<270	32.6	366	8.9
95	5	1.2	<270	54.4	607	8.9
95	5	1.2	<270	76.1	1406	5.4
94	6	1.5	270	54.4	155	35.2
94	6	1.5	270	109	461	23.6
94	6	1.5	270	185	2335	7.9
93	7	1.9	270	109	141	76.9
93	7	1.9	270	163	427	38.2
93	7	1.9	270	218	1615	13.5
90	10	2.4	805	163	182	89.8
90	10	2.4	805	218	407	53.4

[1] Coil 2A , .375 in. tubing

[2] Shear stress and apparent viscosity are based on a calculated flow
length of 1252 cm.

[3] Apparent Reynolds numbers are calculated using apparent viscositie

TABLE V

CHARACTERISTIC FLOW DATA[1] FOR LNG GELS AT 102°K PREPARED USING 2.5 VOL. % WATER GELANT IN THE INJECTION GAS STREAM

LNG 1 Gas) ane	Wt. % Gelant	Yield Stress (dynes/cm^2)	Shear Stress[2] (dynes/cm^2)	Shear Rate (sec^{-1})	Apparent Viscosity[2] (centipoise)	Apparent Reynolds Number[3]
5	1.2	< 270	43.5	393	11.1	126
5	1.2	< 270	54.4	848	6.41	469
7	1.3	< 270	43.5	172	25.3	24.3
7	1.3	< 270	54.4	385	14.1	97.3
7	1.3	< 270	76.1	1194	6.37	669
1	2.0	270	76.1	222	34.4	23.6
1	2.0	270	109	547	19.9	100
1	2.0	270	163	1476	11.1	488

75 in. tubing

s and apparent viscosity are based on a calculated flow coil effective 252 cm.

ynolds numbers are calculated using apparent viscosities.

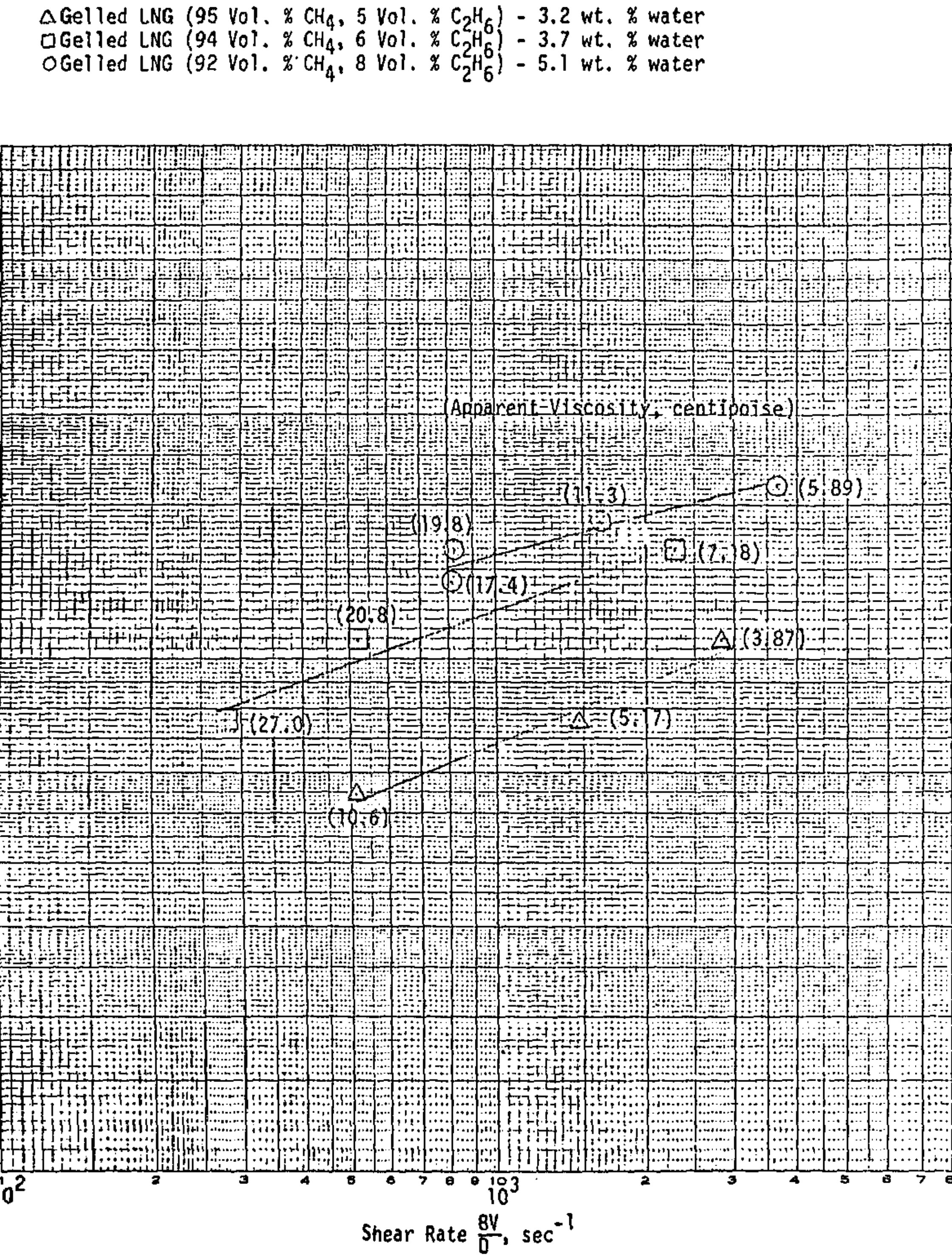
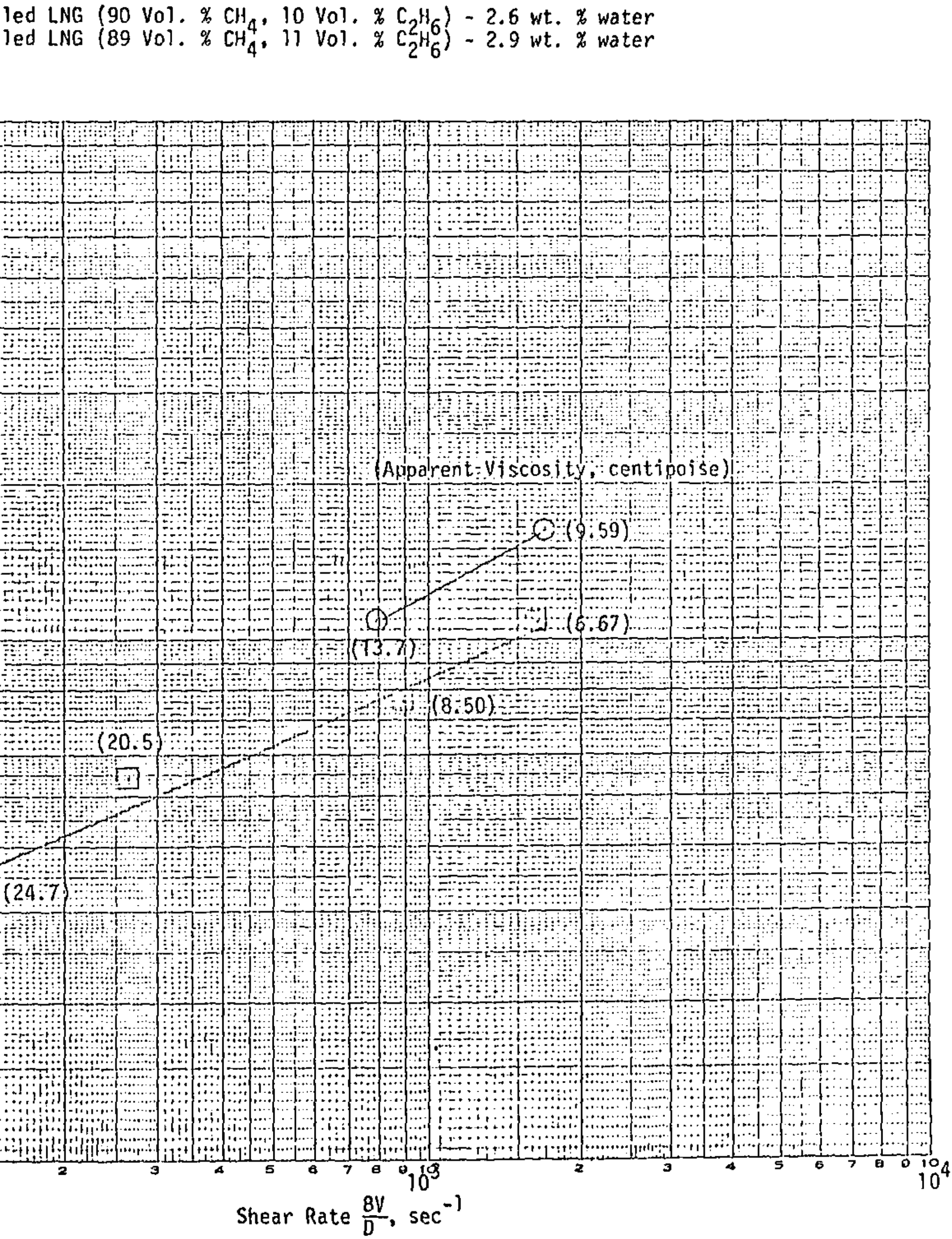


Figure 1. Characteristic Flow Curves of Gelled LNG at 102°K Prepared Using 60 Vol. % Water Gelant in the Injection Gas Stream



ure 2. Characteristic Flow Curves of Gelled LNG at 102°K Prepared Using

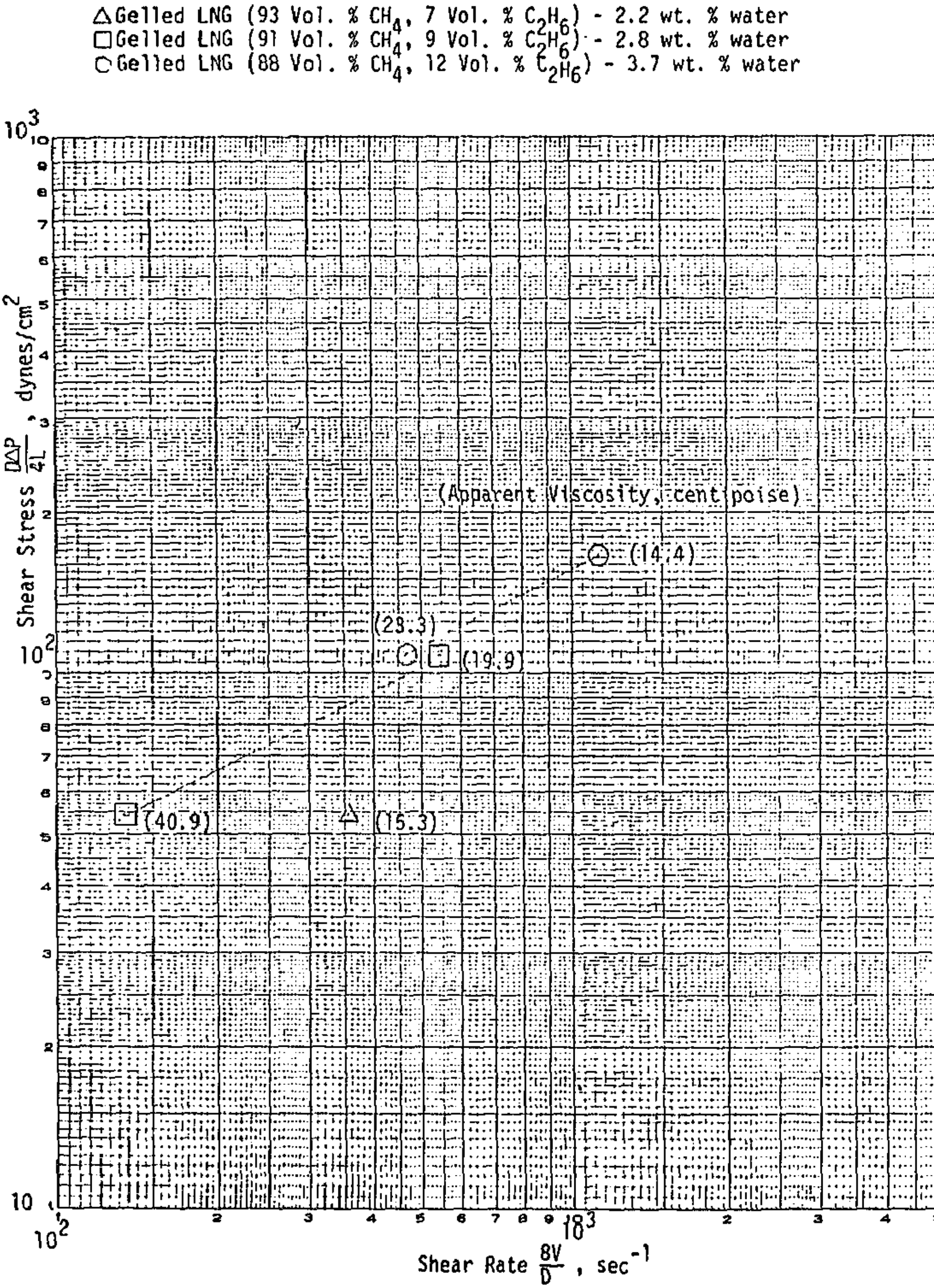
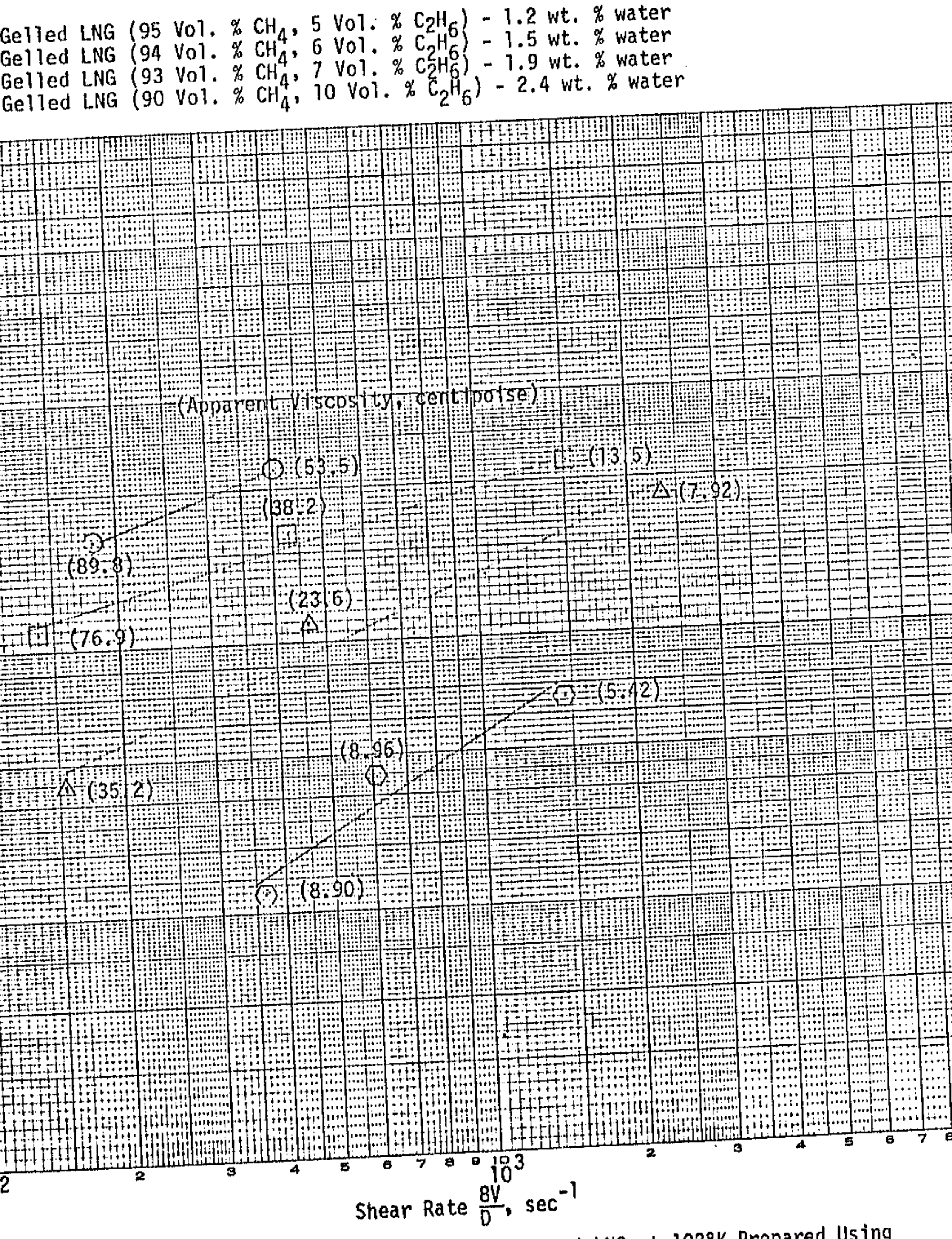
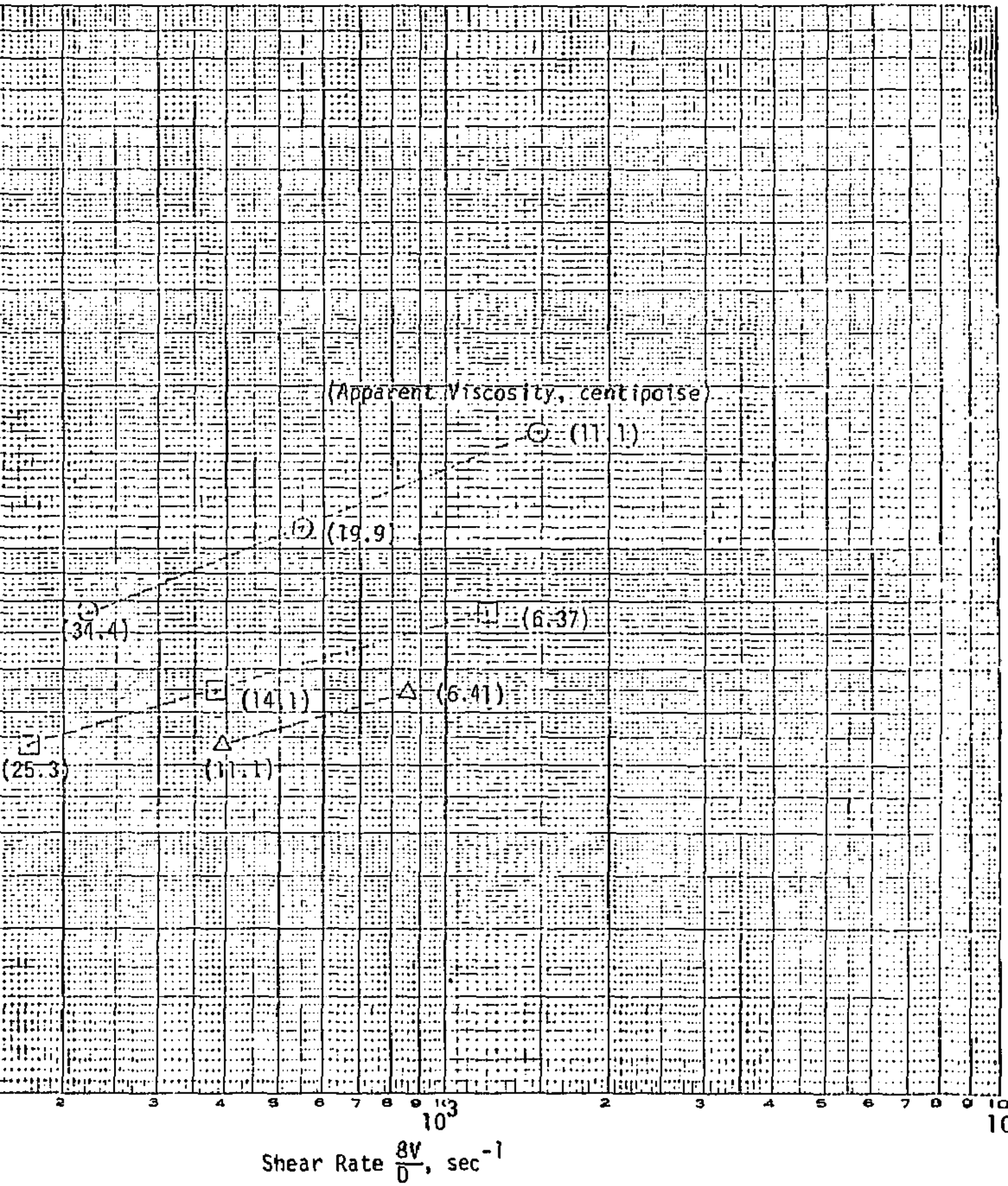


Figure 3. Characteristic Flow Curves of Gelled LNG at 102°K Prepared U
24 Vol. % Water Gelant in the Injection Gas Stream

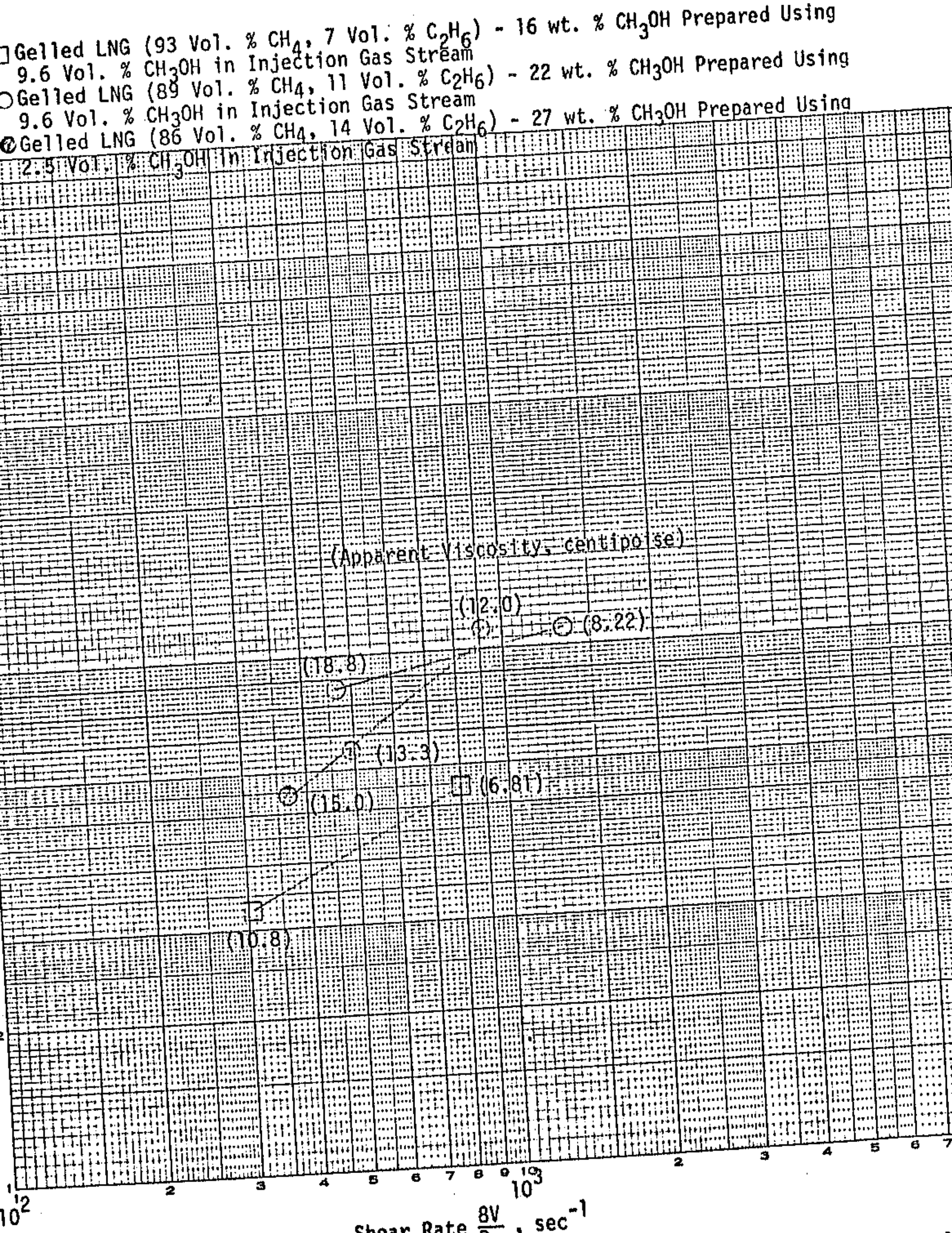


4. Characteristic Flow Curves of Gelled LNG at 102°K Prepared Using

led LNG (94 Vol. % CH_4, 6 Vol. % C_2H_6) - 1.2 wt. % water
led LNG (93 Vol. % CH_4, 7 Vol. % C_2H_6) - 1.3 wt. % water
led LNG (89 Vol. % CH_4, 11 Vol. % C_2H_6) - 2.0 wt. % water



ure 5. Characteristic Flow Curves of Gelled LNG at 102°K Prepared Using



Gelled LNG (93 Vol. % CH_4, 7 Vol. % C_2H_6) - 16 wt. % CH_3OH Prepared Using
9.6 Vol. % CH_3OH in Injection Gas Stream
Gelled LNG (89 Vol. % CH_4, 11 Vol. % C_2H_6) - 22 wt. % CH_3OH Prepared Using
9.6 Vol. % CH_3OH in Injection Gas Stream
Gelled LNG (86 Vol. % CH_4, 14 Vol. % C_2H_6) - 27 wt. % CH_3OH Prepared Using
2.5 Vol. % CH_3OH in Injection Gas Stream
(Apparent Viscosity, centipoise)
(12.0)
(8.22)
(18.8)
(13.3)
(6.81)
(15.0)
(10.8)
10^2
10^3
Shear Rate $\frac{8V}{D}$, sec^{-1}

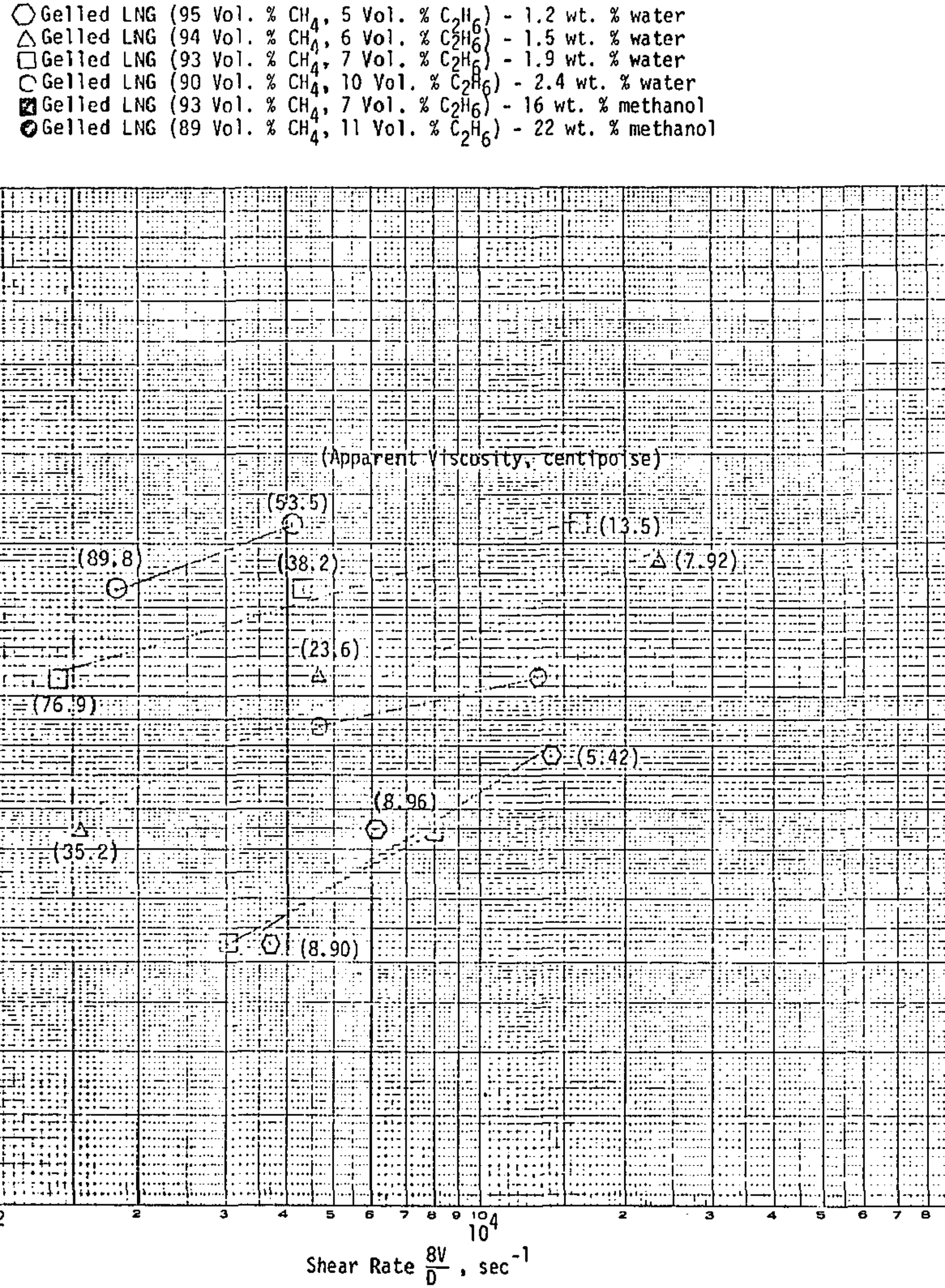


Figure 7. Characteristic Flow Curves of Gelled LNG Using Water Gelant (10 Vol. % in Injection Gas Stream) or Methanol Gelant (9.6% Vol. % in Injection

shear-thinning characteristics.

- For a given injection stream gelant concentration, the d of shear-thinning generally increases with gelant conten This is true for both water gelant type and methanol gel type LNG gels.

In summary, under similar preparation conditions (i.e., similar ion stream gelant concentrations), significantly more methanol than wate uired to obtain LNG gels of comparable yield stress and apparent viscosi s shear rates. This is true over the ranges of gelant content and injec gelant concentration examined in this study. This indicates that wate be considered the superior gelant for applications in which a minimum ant is desirable.

c) Task 3 - Safety Evaluation Tests

The gelation apparatus has been modified so that 5 gallon quanti elled LNG can be prepared and transferred in a temperature-conditioned t The devices to be used in the spill tests are being fabricated and ins use during the next reporting period.

Some simple comparative spill tests have been initiated. The ph elled LNG are shown on Figures 8 and 9. Figure 8 shows white, transluc spilled on a styrofoam pad, photographed two minutes after the spill wa ure 9 shows the same spill 20 minutes after. The photograph shows white ucture still evaporating at a drastically reduced rate. The same amour elled LNG would evaporate in less than 30 seconds.

d) Task 4 - Preliminary Design of Industrial-Scale Gelation Syste

This task is scheduled to start in January of 1979.

Figure 8. Gelled LNG - Land Spill Photographed 2 Minutes afte the Spill.

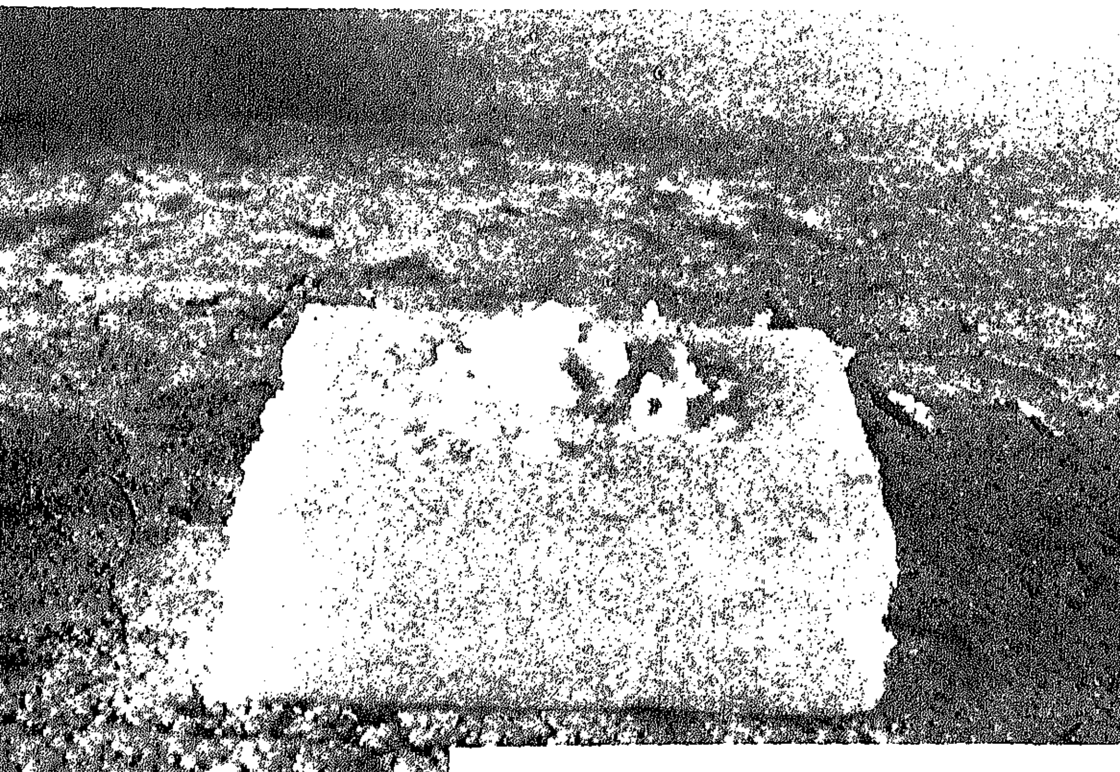


Figure 9. Gelled LNG - Land Spill

e) Task 5 - Preliminary Economic Assessment

One of the program objectives is to evaluate a practical and ercially acceptable means of gelling LNG. Therefore economic analysis o tion process and its integration into the LNG operations has been initia onsidering various approaches to the integration problem, it is necessar ine some of the system implications.

The gelation of the LNG may take in many places; at the liquef nt, at point of embarkation, or at the port of entry.

There are certain advantages of gelling LNG at the baseload li nt. These include the flexibility of using either water or methanol as ability to reliquefy the boil-off resulting from gelation, the vailabi hane as the carrier gas, and the safety from spillage that contributes erall security of the plant. Furthermore, gelation can be accomplished oduct stored on the premises until ready to be transported.

Gelation at the point of embarkation, implies a process, wher IG is gelled as it is loaded on-board the ship. In this case either gro acilities or shipboard facilities can be employed. The boil-off may be shore and used locally, or stored on-board for propulsion, or reliquefie

Gelation at port of entry is perhaps the lease desirable alte n that it defeats the purpose of gelation, which is to provide a safe, product. However, if it is necessary to transport LNG overland, or to s populated area, it may be desirable to use ground facilities for gelling

Only the baseload and peakshaving plants are normally equip liquefaction systems and these plants are prime candidates for implemen the gelation process.

The liquefaction of natural gas involves the removal of its sen latent heats, either by the use of an adiabatic expansion process (the pander" cycle) or by mechanical refrigeration (the mixed refrigerant or le).

The cost of gelation was examined by studying a cascade refrige nt, modified to accept boil-off and cooled down carrier gas from the gel cess. Two modifications were analyzed, one in which the cold gas was us l down incoming natural gas prior to liquefaction of both streams; the o which the cold gas was introduced into the liquefaction process at the l refrigeration. The latter modification appears to be more economical, i se of requiring less total compression energy.

A cursory analysis, based on, as yet, limited data, was conduct boil-off rate due to an open spill and its subsequent atmospheric dispe is anticipated that the lower-boil-off rate of gelled LNG may reduce the tance to the lower flammability limit by at least a factor of five. The lication of this is, that the danger zone can be 1/25 the area of that c a liquid LNG spill.

Current work will determine the energy needed for LNG liquefact ation, define gelation integration and reconstitution process, and evalu ipment changes required for incorporation of the gelation process. Cost itional gelation equipment will be estimated to prepare the overall cost luation and economic assessment of gelation process.

igation of the Suitability of Gelled Methane for Use in a ine," E. M. Vander Wall, Contract NAS3-14305, Report No. -72876, March 1971.

ructure and Rheological Properties of Liquefied Natural led with Water and Methanol Clathrates," L. M. Shanes, Ph.D MIT, August 1977.

REPORT I

Detection of Atmospheric Methane

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FIGURES

TABLES

SUMMARY

This program has as its objective the evaluation and development of accurate, reliable, and rapidly-responding methods for measuring th concentration of methane in the atmosphere. Emphasis is being placed instrument concepts suitable to the detection of methane concentration between 0.1% and 100%, as would be encountered in hazardous spills of LNG or serious ruptures of flammable gas containment vessels.

We are currently completing a prototype instrument suitable for use in field tests of LNG dispersion. The instrument uses a He-Ne las operating at 3.39 μm to produce two beams at slightly different wavelengths. One wavelength is strongly attenuated by methane whereas the other suffers negligible attenuation and serves as an optical intensit reference. The instrument has an on-board microprocessor and digital tape cassette for local data processing and data storage. The entire unit is battery operated and is turned on by a telemetry signal prior to the beginning of the field test. Battery operation allows placemen of the instrument in the test area without the necessity of power and signal cabling or large-bandwidth telemetry systems for data transfer. The analog/digital converter and digital tape can also record voltages from other satellite instruments.

The measurement concepts developed in this program are also appl cable to other gaseous species such as ammonia and LPG. For example, replacing the He-Ne laser with a multiple-line CO_2 laser would produce a system suitable for detecting ammonia.

INTRODUCTION

In June of 1977, the Fluid Mechanics Laboratory at MIT undertook valuation of several alternative methods for accurately measuring the entration of atmospheric methane. The primary alternatives to be stigated were:

- conventional black-body absorption instruments
- optoacoustic spectroscopy
- a two-wavelength He-Ne laser absorption system

g the criteria to be used in evaluating these three methods were the owing:

- cost
- dynamic range
- speed of response
- absolute accuracy (freedom from drift, high signal-to-noise ratio)
- ease of use (infrequent calibration, simple and flexible installation, reliability)
- lack of potential artifacts, particularly in the presence of dust, dirt, and condensed water vapor as in a low-temperature cloud produced by an LNG spill.

n integral part of our program, we also addressed the problem of data isition and processing.

The performance requirements and stringent operating conditions endant to large-scale LNG atmospheric dispersion tests suggested ngly that the two-wavelength laser system was superior in performance but somewhat more costly than, conventional black-body instruments. ough the principles of a two-wavelength He-Ne laser for methane contration measurement were discussed by Moore (1965) and Gerritsen (1966), nstrument using this technique had ever been constructed. We there- expended the dominant fraction of our resources on the two-wavelength er system. This required the development of suitable instrument cons, proof-of-principle tests using a breadboard system, and construction

of a field-usable prototype which will be evaluated by DOE during the coming year.

The prototype is housed in a rugged portable case, is powered internal batteries, and has an on-board microprocessor that controls t instrument functions, acquires raw data from the detectors and convert the data to digital form, calculates light intensity ratios and perfor other algebraic manipulations to determine methane concentration, and stores the results on an on-board digital cassette recorder. Elapsed-time records and other data such as thermocouple temperature measureme may also be stored on the tape. The instrument measures methane conce tration in the ambient external atmosphere at 30 Hz. In circumstances where such detailed data are not required, the microprocessor may be p grammed to compute time-averaged concentrations and record only those averages and the statistical distributions of concentration values abo the averages.

Section 2 describes our preliminary assessment of design requi ments and the advantages and disadvantages of conventional black-body, optoacoustic, and laser-based instruments in meeting these requirement Section 3 presents details of the two-wavelength laser optical system and data relating to optical absorption, obscuration by condensed wate vapor, methods of producing the two wavelengths, and the optical detec tion scheme employed. Section 4 is devoted to a description of the instrument prototype, including the data acquisition system, and inclu data useful in estimating the cost of replication of the instrument in quantity. The last section, 5, presents a critical appraisal of the instrument and compares its performance with other instruments under consideration by DOE for use in future field tests.

OBJECTIVES

evious atmospheric dispersion experiments sponsored by the of Energy, the American Gas Association, U.S. Coast Guard, were useful in establishing the design objectives that a nstrument must meet. Near the origin of the cloud, natural trations would approach 100% whereas in the far-field disper- continual mixing between the gas and the atmosphere would e concentration to values well below flammability limits. concentration of interest depends primarily upon the impor- r-field data in testing analytical dispersion models. We design objective that a suitable instrument should measure e with no greater than ± 5% error. The total dynamic range, the maximum concentration to be measured divided by the maxi- n the smallest concentration, was therefore (100%/0.005%) or

mean methane concentration downwind of a large-scale spill relatively slowly, the relevant time scale being on the seconds. Superimposed on the slow variation of mean methane on are high-frequency fluctuations produced by turbulent mix- obtained from recent tests [Koopman (1978)] as well as esti- e spatial scale of turbulent fluctuations [Dewey (1977a)] t concentration fluctuations as large as a factor of two can mes of the order of 0.03-0.1 sec. The desired instrument se will therefore depend upon the information required from a l eddies containing flammable concentrations of methane may dispersed plume whose mean concentration is substantially n the lower flammability limit. In order to establish the of the turbulent concentration fluctuations, a response time bout 0.1 sec is required; this design specification was assessing alternative instrument concepts.

uracy and freedom from systematic artifacts are also important Even with low ambient humidity, water vapor condensation (fog) ny a wide range of methane concentrations. Optical methods

are particularly sensitive to aerosol scattering because one must distinguish between scattering and methane absorption. A heated sampling t would eliminate this problem, but at the expense of additional electr power, a lag time between sample extraction and instrument reading, a potential artifacts from evaporation of macroscopic water drops. In recent test (LNG-18, China Lake, 8/31/78), substantial condensation w apparent at methane concentrations above about 14%, even though the a ent temperature was high (35.8°C) and the relative humidity was low (Optical attenuation would occur at even lower concentrations with hig ambient humidity.

One method of eliminating errors in concentration measurement caused by aerosols is to use two specific wavelengths, one being coin dent with an absorption line of the species being measured and the ot in a spectral region in which no absorption occurs. This mode of ope tion can be described with a simple calculation. If the absorption w length is λ_1 and the incident and transmitted intensities are I_{01} and respectively, and it is further assumed that the absorption follows B law with an absorption coefficient σ_1 (cm^{-1} atm^{-1}), then

$$\frac{I_{01}}{I_1} = e^{(\sigma_1 c + s_1)x} \equiv R_1$$

where c is the concentration of absorbing gas (atm), x is the total p length (cm), and s_1 is an aerosol scattering coefficient (cm^{-1}) at wa length λ_1. If a second wavelength λ_2 is scattered but not absorbed,

$$\frac{I_{02}}{I_2} = e^{s_2 x} \equiv R_2$$

If λ_1 and λ_2 are sufficiently close together or if the individual dro lets are very large compared to λ_1 and λ_2, then $s_1 = s_2$ and c may be determined from

$$c = \frac{\ln[R_1/R_2]}{\sigma_1 x}$$

If R_1 and R_2 are measured, c may be determined from Eq. (3) even in t presence of substantial aerosol scattering. The key requirement, how is that $s_1 = s_2$. This condition is violated if λ_1 and λ_2 are far apa Note that the transmitted intensities I_1 and I_2 can be substantially

duced by aerosol scattering, and systems with limited source intensit
ll suffer a substantial decrease in signal/noise ratio.

We now consider the capabilities of a two-wavelength black-body
osorption instrument in meeting the design criteria outlined in this
ection. We consider specifically a system in which narrow-band multi-
ayer dielectric filters are used to obtain narrow wavelength intervals
entered at the two wavelengths λ_1 and λ_2. The most favorable absorpti
avelength λ_1 for methane measurement is 3.4 μm, and the apparent absor
ion coefficient σ_1 is about 0.092 cm^{-1} atm^{-1}. From Eq. (1), a 30 cm
ath length will yield 42% absorption at c = 0.2 atm and 1.4% absorptio
t c = 0.005 atm. Because of the limited source intensity transmitted
y the narrow-band filters, it is difficult to obtain simultaneously a
igh S/N ratio and a fast instrument response. This limitation is
exacerbated by the presence of aerosol scattering.

Our previous experience with black-body sources, narrow-band multi-layer dielectric filters, and pyroelectric detectors suggests tha response times of 3 Hz and signal/noise ratios of 200:1 may be achieved under optimum conditions. An instrument designed for rapid CO_2 measure-ment is being developed at Lawrence Livermore Laboratory [Bingham *et al.* (1978)], and it is claimed that 10 Hz frequency response and a signal/noise ratio of 3000:1 can be achieved. This level of performance is qu exceptional and demonstration of such performance under field condition would suggest that a black-body could meet the accuracy and response ti requirements listed previously using the LLL instrument with filters appropriate to the measurement of methane. In order to achieve the dynamic range requirement, the path length must be altered during the dispersion test. Also, substantial optical scattering, either from dus or aerosols, would significantly decrease I_1 and the signal/noise ratio could decrease to unacceptable levels.

Our calculations suggest that there is a significant potential error that could be introduced by aerosol scattering in an instrument using a black-body source and multi-layer dielectric filters. For pur-poses of illustration, we take the measuring wavelength λ_1 to be 3.40 μm

(i.e. $\nu_1 = \lambda_1^{-1} = 2941$ cm^{-1}), $\sigma_1 = 0.092$ cm^{-1} atm^{-1}, $\lambda_2 = 3.85$ µm (ν_2 = 2597 cm^{-1}), and $\sigma_2 = 0$. If the aerosol scattering scales according t the Rayleigh scattering formula, then the scattering coefficients s_1 s_2 at λ_1 and λ_2 are related by

$$\frac{s_1}{s_2} = (\nu_1^4/\nu_2^4)$$

We have measured values of s_1 between 0.12 cm^{-1} (visibly transparent and 0.34 cm^{-1} (very thick fogs). Taking $s_1 = 0.2$ cm^{-1}, the differenti scattering coefficient is

$$s_1 - s_2 = 0.2\left(\frac{\nu_1^4 - \nu_2^4}{\nu_1^4}\right)$$
$$= 0.078 \text{ cm}^{-1}$$

Thus, the differential scattering coefficient may be equal to or larg than the attenuation $\sigma_1 c$ arising from the presence of methane. Even lower humidity, a weaker dependence of the aerosol scattering coeffic upon wavelength, and a choice of filter center wavelengths λ_1 and λ_2 are closer together, significant errors can arise.

Optoacoustic spectroscopy [e.g. Dewey (1975,1977b)] offers th advantage of large dynamic range but is useful primarily at low conce trations on the order of 1-1000 ppm; use at higher concentrations wou require accurate dilution of the sample and this would entail additio instrument complexity as well as reducing the speed of instrument res to concentration changes.

A two-wavelength laser system offers many advantages over bla body and optoacoustic methods of measuring high concentrations of met The two wavelengths λ_1 and λ_2 differ by only 3 parts in 10,000 and th reduces differential aerosol scattering to a negligible level. Radia intensity at the detector is several orders of magnitude larger than intensity available from conventional black-body sources, thus increa the signal/noise ratio. The optical alignment of the system is considerably simplified because the source beam is collimated and of sma diameter. The methane absorption coefficient at the measuring wavele

is about a factor of 100 larger than that observed with a black-body so and narrow-band filter because the filter "averages" over a series of discrete and widely-spaced methane absorption lines whereas the laser wavelength is coincident with a single vibration-rotation line; this allows much shorter absorption path lengths to be used. And the attenu tion of the laser by methane accurately follows Beer's law (Eq. 1) wher substantial deviations from Beer's law are evident in black-body absorp tion systems designed for a wide range of concentrations.

3. TWO-WAVELENGTH LASER SYSTEM

Although two-wavelength methods have been used for many years i infrared analyzers [see Bartz and Ruhl (1966)], Gerritson (1966) was th first to point out the suitability of the He-Ne laser in this context. A He-Ne laser with broadband mirrors will support numerous laser lines shown in Figure 1. The He energy states are included in the diagram since the energy transport mechanism to Ne is through the electronicall excited He gas. There are three laser lines which operate in cascade; the wavelengths of these lines are 3.39 μm; 2.39 μm, and 1.15 μm (Rosenberger, 1964). Moore (1965) observed that two distinct laser lin could be extracted in the vicinity of 3.39 μm. Without intracavity attenuation, laser action is obtained at ν_1(vac) = 2947.903 cm^{-1}; if a cell containing methane is inserted into the cavity, lasing occurs at ν_2(vac) = 2948.790 cm^{-1}. Gerritsen reasoned that methane absorbs strongly at ν_1 and only weakly at ν_2. Therefore, these two lines could be used, respectively, as measurement and reference wavelengths. Moore measurements demonstrated that ν_1 coincided almost exactly with the kno position of the P_7 line of methane (ν_3 vibration band) centered at 2947.9 cm^{-1}.

The two-wavelength method proposed by Gerritsen forms the basis of the instrument system we have developed. Gerritsen's original sug- gestion of using a methane-filled gas-cell mounted radially and opposin an empty gas cell on an intracavity rotation wheel was deemed to be an impractical method of producing alternating outputs at ν_1 and ν_2.

ACKNOWLEDGMENT

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gram originated in the Division of Environmental Control Technology,
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U.S. Department of Commerce
 Maritime Administration

U.S. Department of Transportation
 Coast Guard
 Federal Railroad Administration
 Office of Pipeline Safety Regulations

National Aeronautics and Space Administration

The Fertilizer Institute

The Gas Research Institute

This document was compiled by Pacific Northwest Laboratory, operated b
telle Memorial Institute, who is assisting the Division of Environmenta
trol Technology in the development and planning of this program.

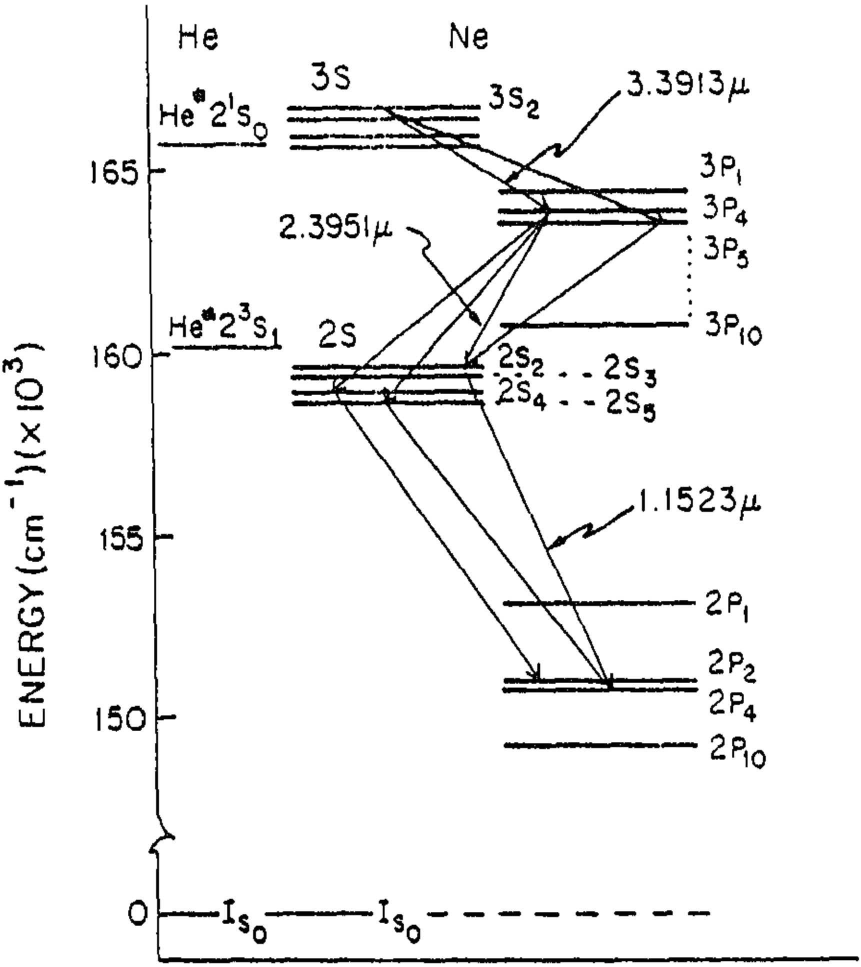


Figure 1. Ne energy diagram for a cascading laser system [after Rosenberger (1964)].

refore, a substantial amount of effort was expended to find suitable ernative methods of selecting ν_1 and ν_2 that were superior to the ating cell arrangement.

One method investigated uses a Glan-air polarizing prism to ect two independent arms of the laser cavity. A specific embodiment shown in Figure 2. Radiation polarized in the plane of the drawing polarization) will traverse the polarizing prism with negligible loss, reas radiation polarized in a plane perpendicular to the drawing (S-arization) will be totally reflected at the internal prism interface emerge at an angle with respect to the original cavity axis. Two ependent optical cavities that will support lasing on opposite polari-ions may therefore be formed by terminating the two polarized beams rging from the prism with reflective mirrors. If a methane cell is ced in the P-polarization arm, the laser will provide P-polarized iation at ν_2 and S-polarized radiation at ν_1. By alternately blocking of the two paths with a simple rotating mechanical chopper, the laser l alternate between ν_1 and ν_2. The advantage of the polarizing prism hod over a simple arrangement using a beam splitter is that 100% of laser's power can be extracted whereas a beam splitter system will duce much less than 50% of the power on either line. The system is hanically simpler than the rotating methane filled gas cells, but has been tested to date because of delays in manufacture of the prism by outside vendor.

An alternative piezoelectric crystal system was considered; this tem shown in Figure 3 uses a polarizing prism as in Figure 2, and adds arizing laser tube windows, but it eliminates the mechanical rotating pper cone by using a polarization rotator. If a voltage is applied oss a piezoelectric crystal while it is in front of the polarizing sm, the crystal will contract or expand in proportion to the applied tage (typical required voltages are 200 volts/μm motion for a 4 mm ck crystal). These crystals exhibit large strain-induced birefringence; polarization of an incoming beam can be rotated by changing the thick-s of the crystal through the applied voltage. With the application

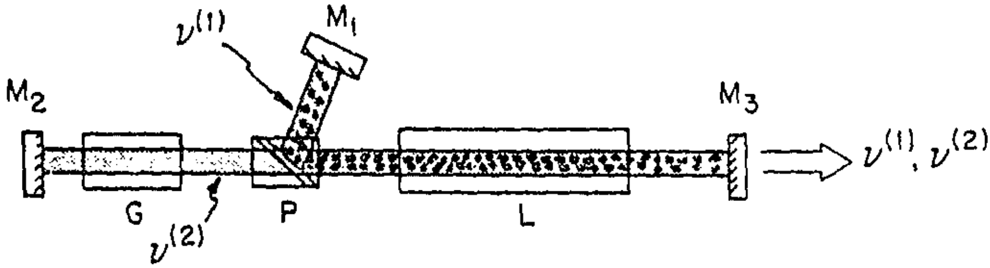


Figure 2. Two-wavelength laser using a polarizing prism [Dewey (1978)].

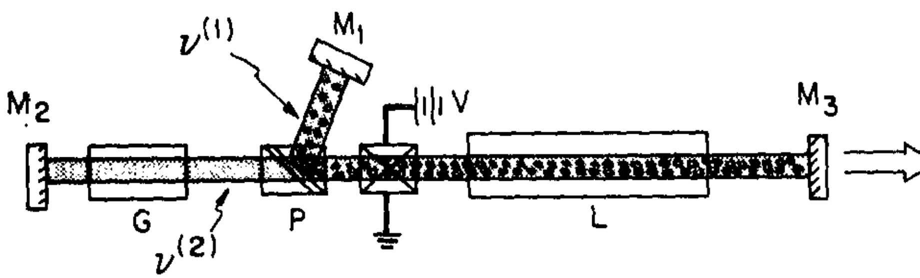
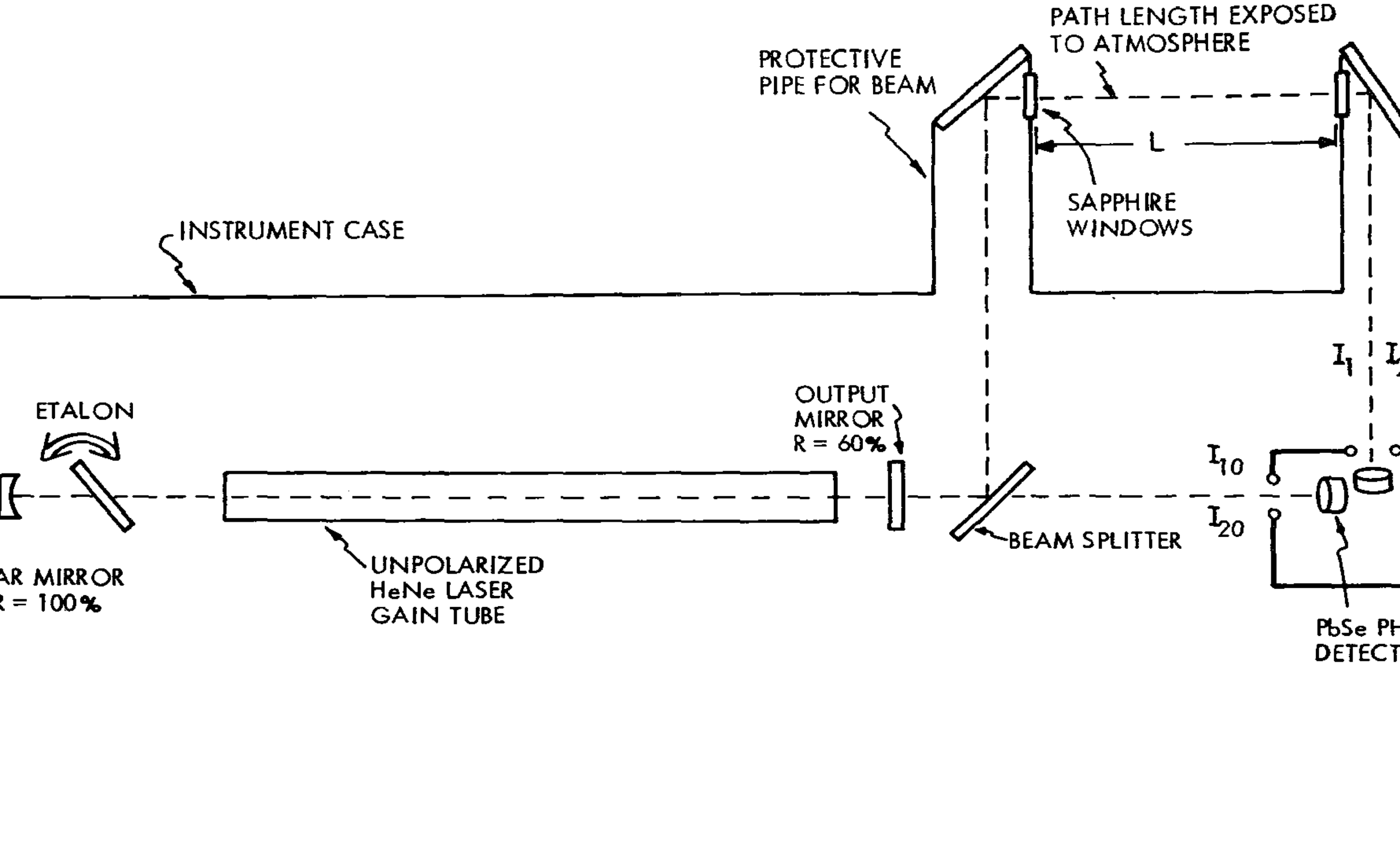


Figure 3. Two-wavelength laser using a polarizing prism and polarization rotator.

alternating voltage, the polarized beam from the laser can be rota- either look like a S or a P polarization, thereby being transmitted ected appropriately by the polarizing prism. Consequently this chops between ν_1 and ν_2 electrically, eliminating the need for a ical chopper. Potential problems with this system lie in its reli- a 100 Hz high-voltage (about 1 kV) control system.

The final system, and the one adopted for use in our prototype, till another method to alternate between ν_1 and ν_2: an intra- Fabry-Perot etalon. As the angle of the etalon changes relative eam of light, the effective thickness changes which varies the lifference between the first reflected wave and the second reflected or analogously the transmitted wave). If the path length between reflecting surfaces is an integral number of half wavelengths, ase lag between reflections at the two surfaces is 180° and 100% ission occurs. Consequently, as the etalon is scanned through a of angles with the incident wavelength fixed, there will be par- angles where the phase lag is 180° so that no reflection occurs. num in transmission occurs for angles intermediate to the peaks. ropriate choice of the etalon thickness, it is possible to make gle for maximum transmission of one wavelength coincide with mini- ansmission at a second wavelength. In our instrument the etalon is ed to transmit ν_2 and suppress ν_1 at one angle and to transmit ν_1 ppress ν_2 at a second angle. If the transmittance is low enough ibit lasing on the ν_1 line, then ν_2 will lase since it sees 100% ittance. A voltage-controlled optical scanner under control of croprocessor is used to alternate the etalon angle between a posi- roducing radiation at ν_1 and one producing radiation at ν_2. The l design is illustrated in Figure 4.

A bread-board model of the laser system shown in Figure 4 was ucted to verify the operation of the etalon, to obtain detailed tion data at ν_1 and ν_2 for methane and other constituents of natural nd to experimentally verify the insensitivity of the concentration ement scheme (see Eq. 3) to substantial aerosol scattering.



ure 4. Overall sketch of instrument configuration using a Fabry-Perot etalon as the wavelength-selection

tails of these results may be found in the thesis of Russ (1978), and
s results are summarized below.

Table 1 lists the measured absorption coefficients at ν_1 (2947.90
$^{-1}$) and ν_2 (2948.790 cm^{-1}) for methane and other hydrocarbons typicall
resent in natural gas. In calculating the overall absorption by a mix-
ure of known concentration, Eq. (1) must be modified to account for the
ifferent species present in the mixture. The total natural gas concen-
ration, C_g, is given by

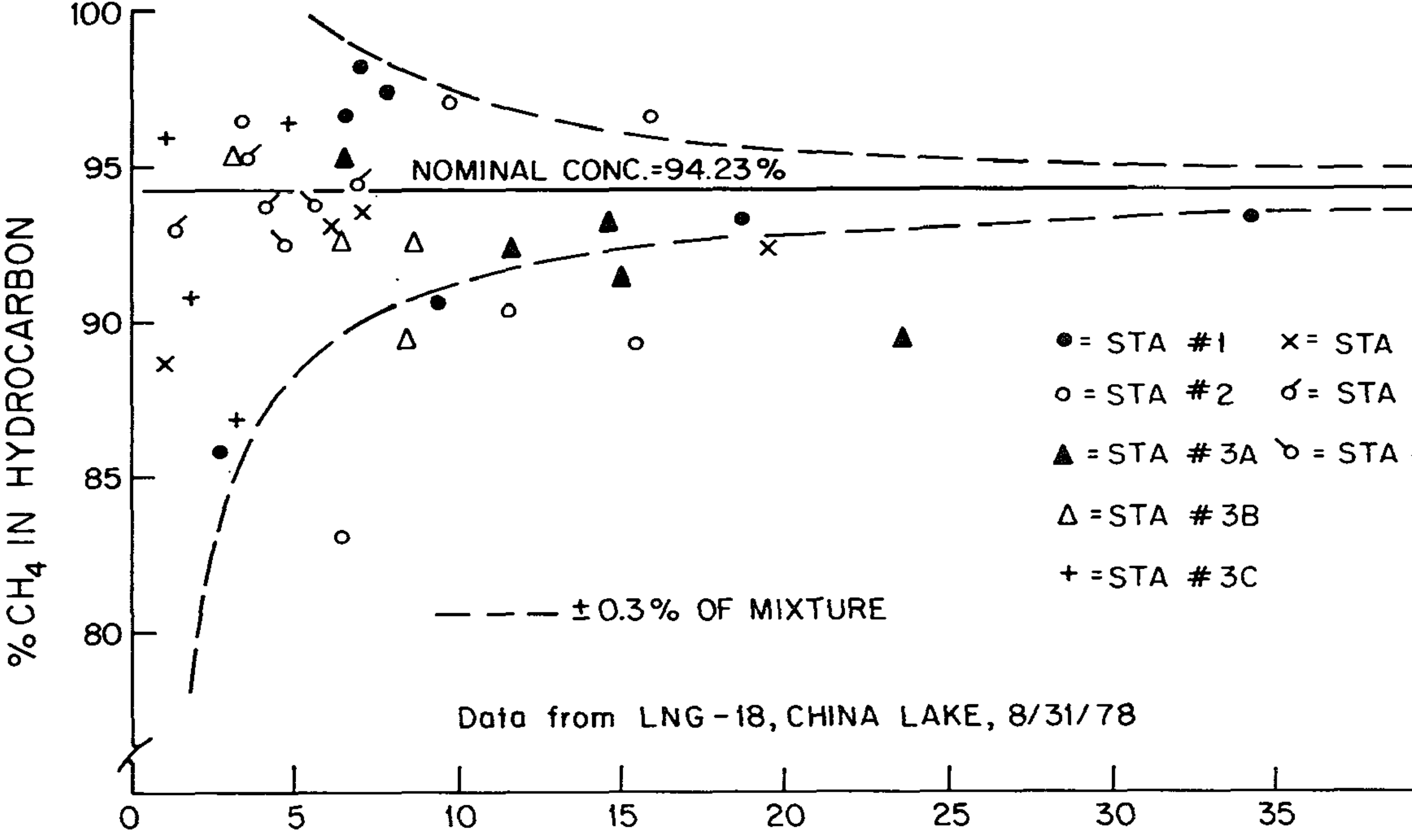
$$C_g = \frac{\ln(R_1/R_2)}{x \sum_{i-1}^{n} (\sigma_{1i}-\sigma_{2i})Y_i} \quad (5)$$

where R_1 and R_2 are given by

$$R_1 = (I_{01}/I_1)$$
$$R_2 = (I_{02}/I_2) \quad (6$$

σ_{1i} and σ_{2i} are the absorption coefficients of species i at ν_1 and ν_2, respectively, x is the absorption path length, and Y_i is the compositi fraction of species i.

Eq. (5) suggests a potential error in the two-wavelength measu scheme. In order to accurately assess the total natural gas concentra using Eq. (5), the specie fractions Y_i must be known. If the composit of the evaporating gas changes during the test, for example because lighter hydrocarbons boil off more rapidly than heavier fractons duri the early portions of a spill, then a systematic error will be incurr Data that bears on this question was obtained during LNG spill test LNG-18 at China Lake in August of this year [Koopman (1978)]. Grab samples taken during the test at various downwind locations were anal using a mass spectrometer to determine the fractions of methane, etha and propane present. From these data we have computed the amount of methane present as a fraction of the total hydrocarbons present. Th results are given in Fig. 5. No systematic variation of methane con tration with either sampling station location or total hydrocarbon c



% CH_4 IN HYDROCARBON
100
95
90
85
80
0
5
10
15
20
25
30
35
NOMINAL CONC.=94.23%
● = STA #1
○ = STA #2
▲ = STA #3A
Δ = STA #3B
+ = STA #3C
× = STA
= STA
= STA
±0.3% OF MIXTURE
Data from LNG-18, CHINA LAKE, 8/31/78

Table 1

Typical Absorption Coefficients of ν_1 and ν_2

of all Major Natural Gas Constituents

	% of Mixture	$\sigma_1(atm^{-1}\ cm^{-1})$	$\sigma_2(atm^{-1}\ cm^{-1})$
methane	87	8.1	.69
ethane	8	8.04	4.64
propane	2	11.6	10.7
n-butane	1/2	13.5	13.1
iso-butane	1/2	13.1	14.9
nitrogen	2	0	0

is apparent. A reasonable hypothesis is that the violent mixing occur
during the boil-off process thoroughly mixes the LNG and promotes form
tion of many fine droplets that subsequently evaporate. Once the dis-
persed droplets evaporate, the relative hydrocarbon fractions in the m
ture do not change because the differential diffusion rates of light
and heavy hydrocarbons are insignificant compared to the turbulent mix
rates.

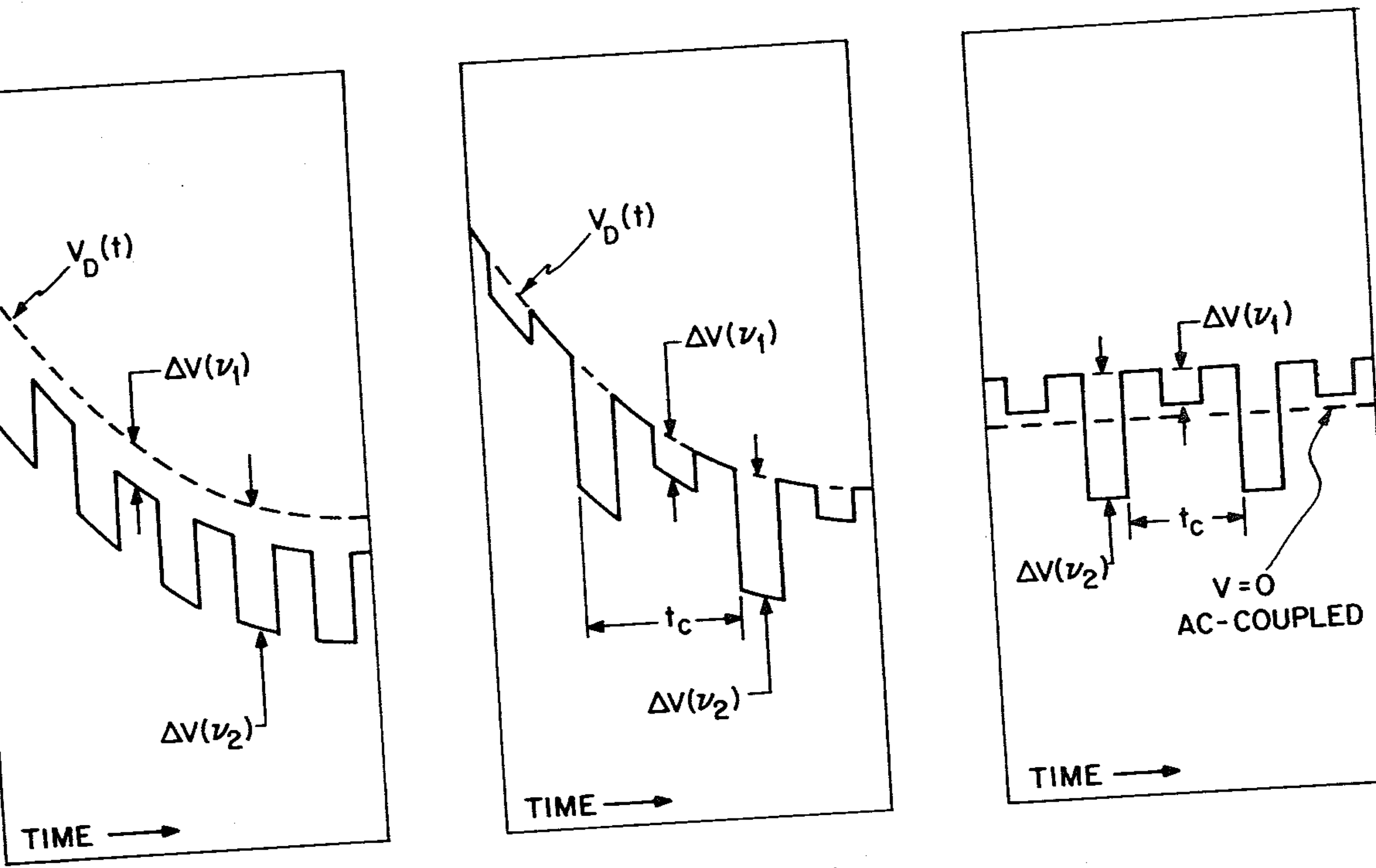
A series of experiments were performed to verify the insensit
of the two-wavelength laser system to the presence of aerosol scatter
Thick fogs of condensed water vapor were produced by pouring boiling
water on liquid nitrogen. The fog was introduced into a 14 cm open s
tion between the laser and the optical detector. The intensity rati
R_1 and R_2 were measured during 20 tests in which the observed scatte
coefficients s_1 and s_2 varied from zero to 0.12 cm^{-1} (visibly transp
fog) to 0.34 cm^{-1} (visibly opaque fog). In all cases, the measured
of s_1 and s_2 were indistinguishable. This is consistent with our th
etical expectations. Even in the extreme case of Rayleigh scatteri
(Eq. 4) with the maximum observed attenuation coefficients $s_1 \cong s_2$ =
0.34 cm^{-1}, the predicted difference between s_1 and s_2 is

$$\Delta s = s_1 - s_2 = 0.34 \ \frac{\nu_1^4 - \nu_2^4}{\nu_1^4}$$

absorption that would be expected in the presence of fog. Even with extremely humid test conditions, fog would not be present for methane concentrations below 2%, and therefore the minimum value of $\sigma_1 c$ in the presence of fog is 16×10^{-2} cm^{-1}, or about 40 times larger than the maximum value of Δs.

The optical detectors we use are 2 mm × 2 mm uncooled PbSe flakes. The detectors are operated in a photoconductive mode such tha small changes in detector resistance caused by incident light are measured. Because detector resistance is also sensitive to detector temp ature, an AC-coupled detection scheme 's employed (Fig. 6c). The intr cavity etalon is designed so that the laser output occurs at ν_1 at one angle θ_1, at ν_2 for a second angle θ_2, and lasing is absent entirely a an intermediate angle θ_0. The microprocessor applies sequential volta to the scanner to produce a sequence of angular positions θ_1, θ_0, θ_2, θ_1, θ_0, ... The resulting detector signal is shown in Fig. 6. Indi measurement sequences (θ_1, θ_0, θ_2, θ_0) occur at 30 Hz, and the effects detector thermal drift are negligible.

The most difficult problem we have encountered with the laser the design of a successful etalon. It has proven difficult to obtain etalon that will have sufficient finesse to allow lasing at ν_1 and ν_2 the two angular positions θ_1 and θ_2 while also inhibiting lasing entir at the intermediate angle θ_0. The primary difficulty has been very lo lead times to fabricate and coat experimental etalons to test specific design parameters rather than any intrinsic physical limitation to the design. We have been reluctant to go to extremely high finesse etalon because absorption and scattering in the coatings and materials then become important. It also becomes increasingly difficult to precisely the angles θ_1, θ_2, θ_0 as the finesse increases. A microprocessor subr tine is used to follow the slow variation of θ_1, θ_2, and θ_0 with etalo temperature.

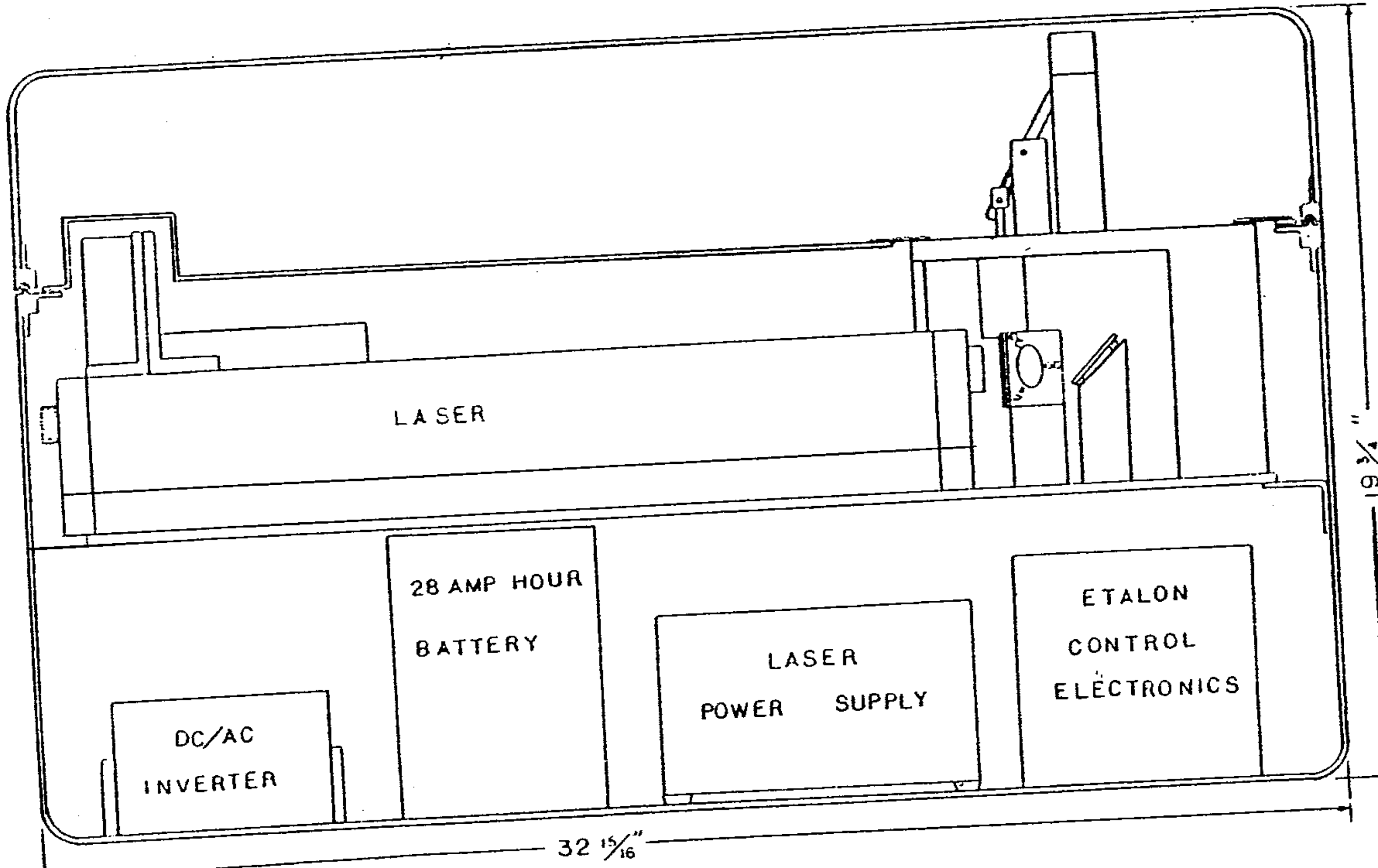


V_D(t)
ΔV(ν_1)
ΔV(ν_2)
TIME
V_D(t)
ΔV(ν_1)
t_c
ΔV(ν_2)
TIME
ΔV(ν_1)
ΔV(ν_2)
t_c
V = O
AC-COUPLED
TIME

Figs. 7 and 8 are schematic drawings [Stein (1978)] of the prototype instrument configuration and Figs. 9 and 10 are photographs of the partially-assembled instrument. Final software development and instrument checkout is now in progress. It is anticipated that the prototype will be shipped to Lawrence Livermore Laboratory for evaluation by DOE personnel early in 1979.

A block diagram of the instrument electronic components is given in Fig. 11. Intensities I_1 and I_2 are measured by detector No. 1 that placed at the end of the optical path that includes the measuring secti This measuring section is defined by the two windows on the upright arm of the "periscope" clearly visible in Figs. 8, 9, and 10. Reference intensities I_{01} and I_{02} are measured by a second detector located near the laser. These two reference intensities are obtained by placing a 10% beam splitter in the beam as it emerges from the laser. It is not necessary to use the same detector to measure all four intensities; the only requirement is that the two detectors have responses that are linearly proportional to the received intensity.

Even with the large light intensity available from the laser, it it not possible to achieve a satisfactory signal/noise ratio over th entire dynamic range of measurement required by this application. We therefore have designed a solenoid-operated lever mechanism that will insert and remove a transparent rod from the atmospheric optical path during the conduct of the test. This rod is visible in Fig. 8. The rod reduces the effective optical path open to the atmosphere to 0.5 cm. For methane concentrations less than the explosive limit, a 10 cm path is required to obtain an optical absorption sufficiently large to yield accurate concentration measurements. Inasmuch as the actual methane concentration is continually computed by the microprocessor, th solenoid retraction mechanism can be automatically activated by the microprocessor when the concentration reaches a predetermined value.


LASER
28 AMP HOUR
BATTERY
LASER
POWER SUPPLY
ETALON
CONTROL
ELECTRONICS
DC/AC
INVERTER
32 15/16"
19 3/4"

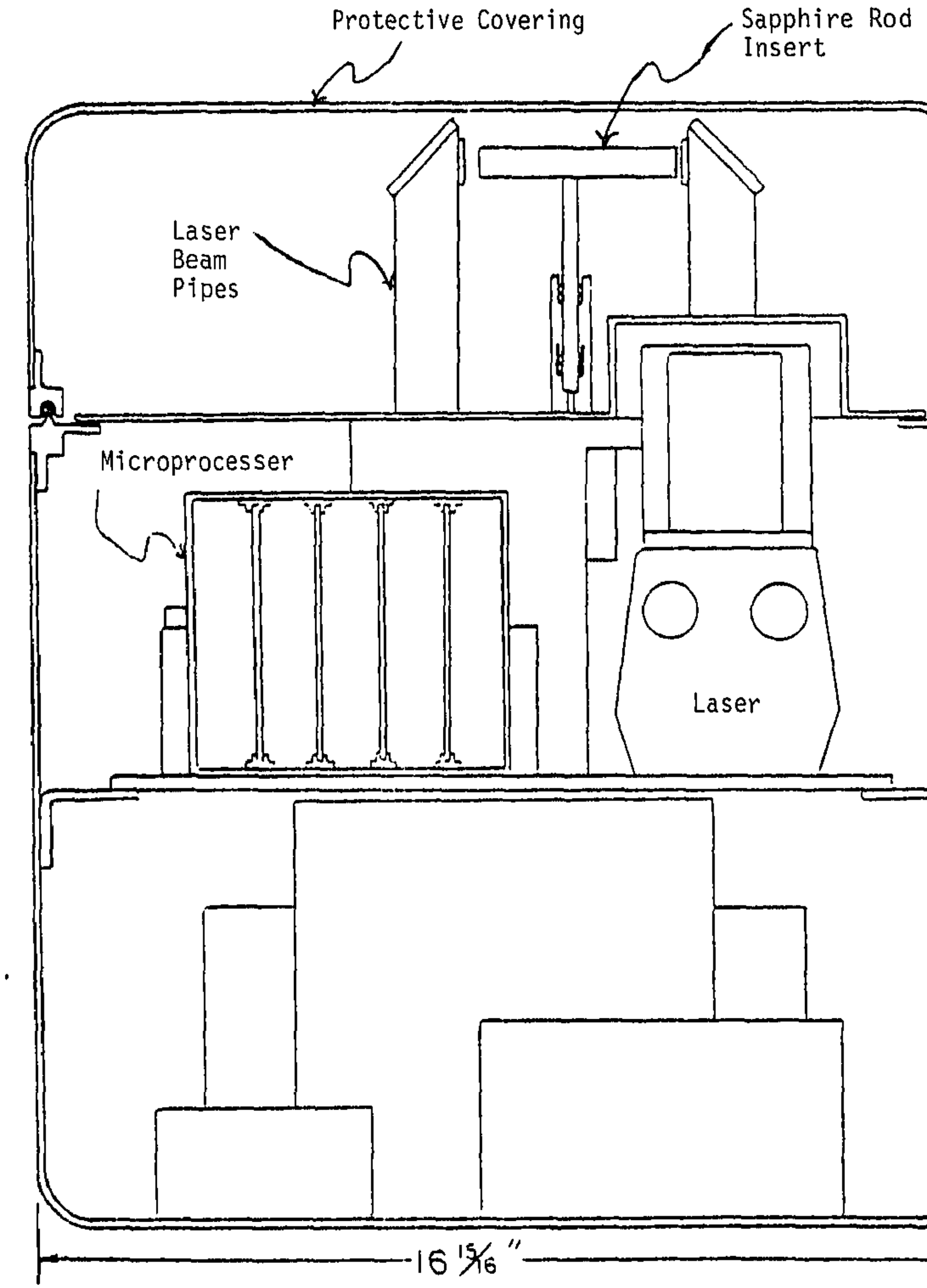
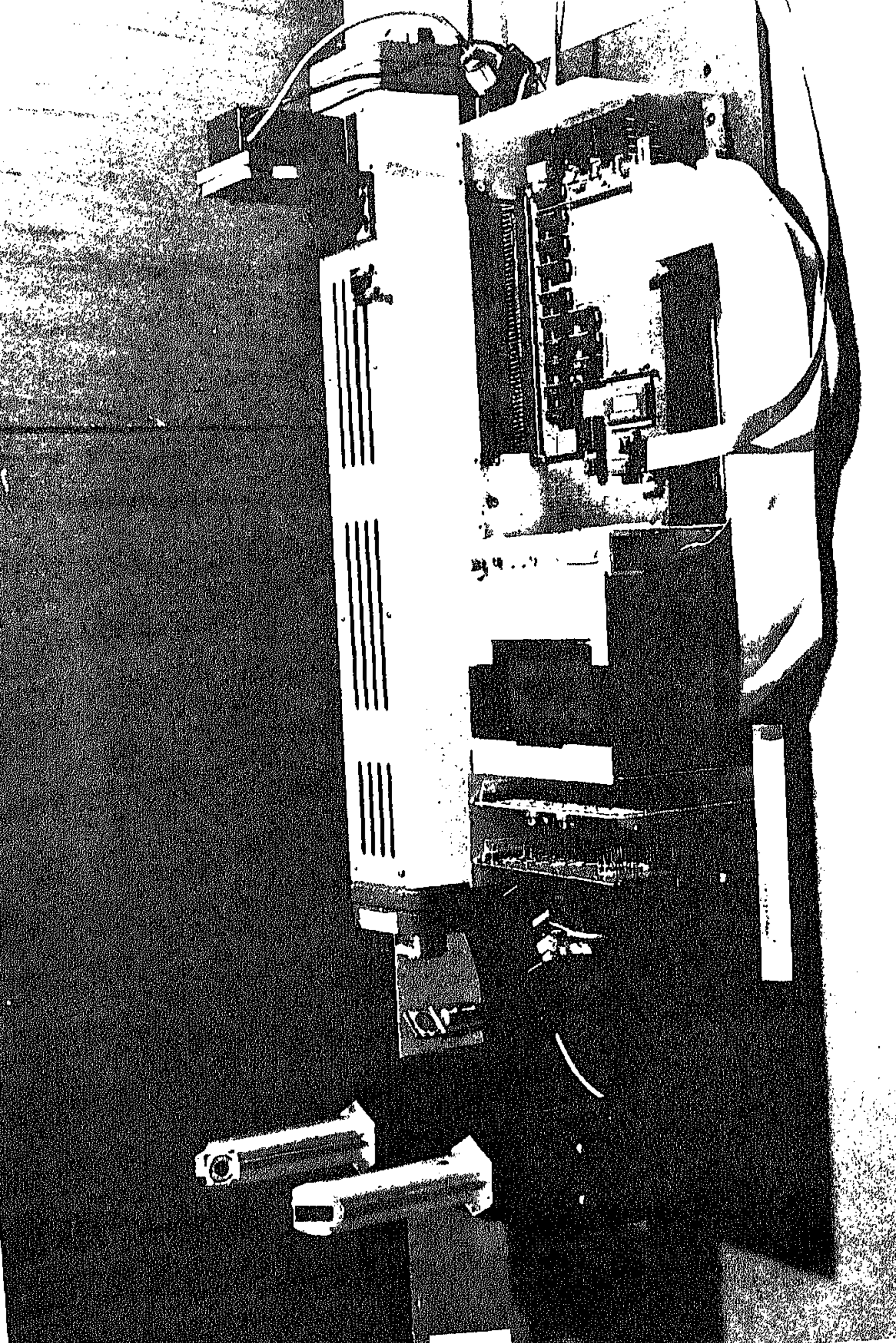
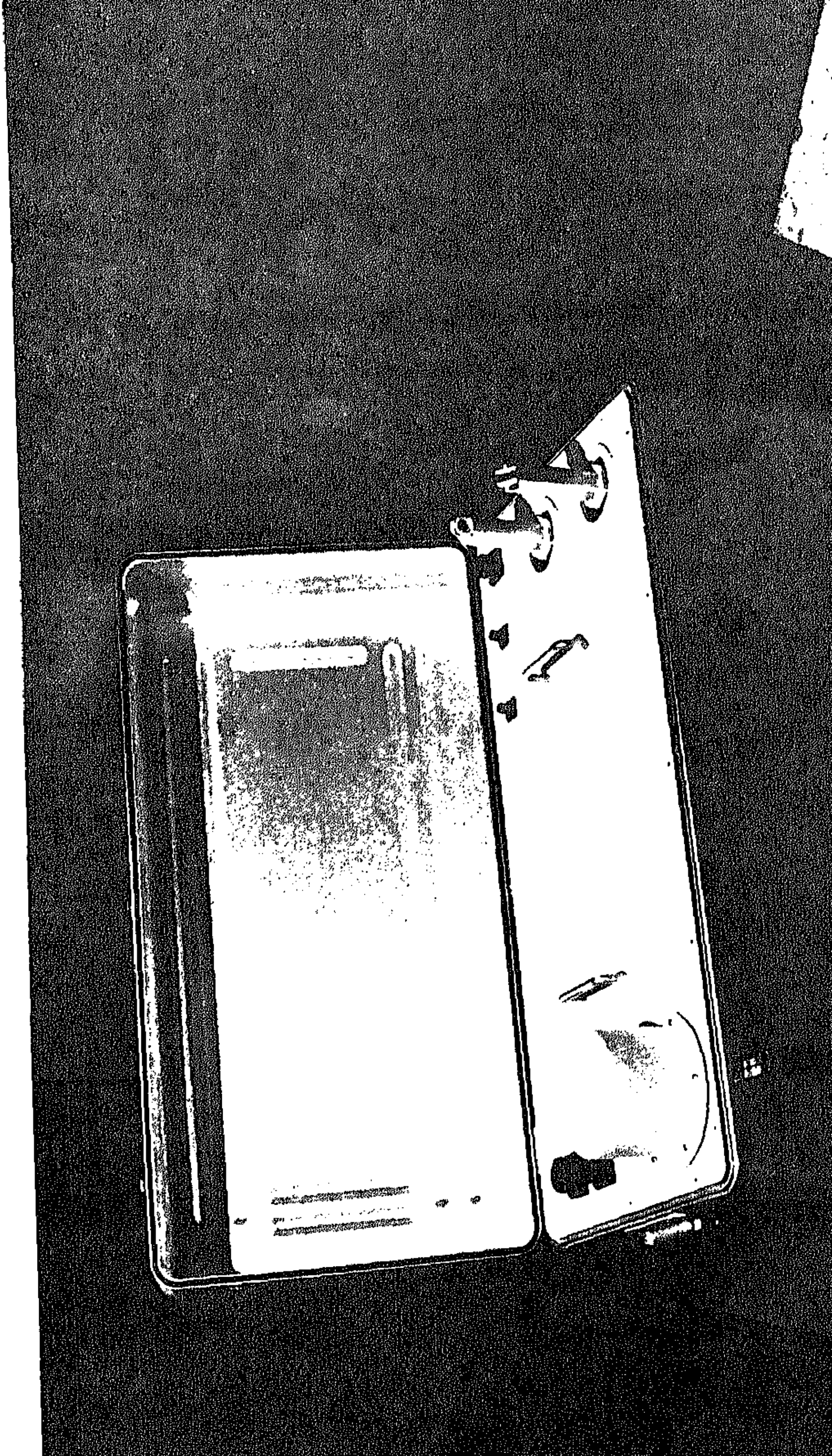
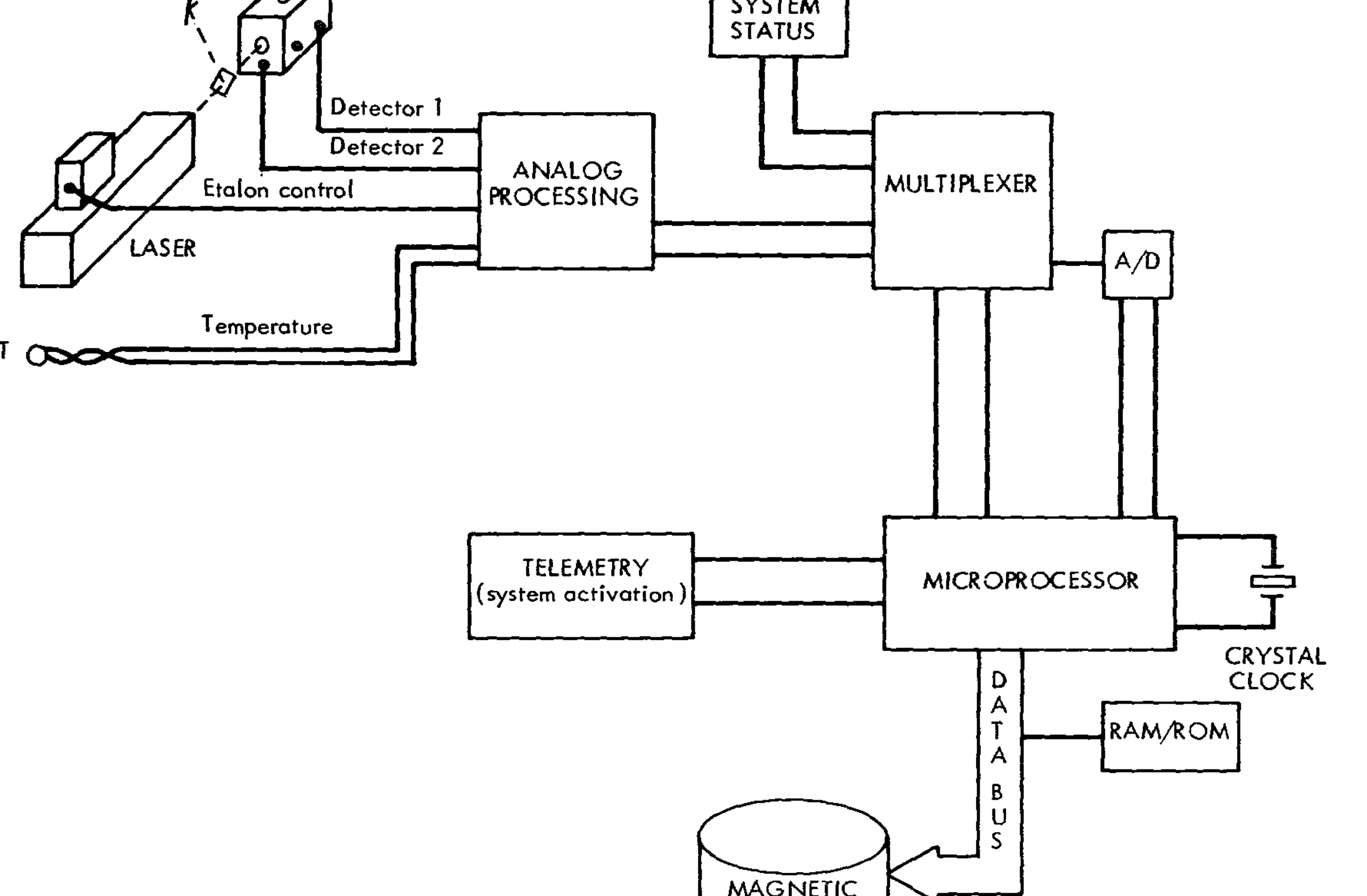


Figure 8. Side view of laser system assembly.






SYSTEM
STATUS
Detector 1
Detector 2
Etalon control
ANALOG
PROCESSING
MULTIPLEXER
LASER
A/D
Temperature
T
TELEMETRY
(system activation)
MICROPROCESSOR
CRYSTAL
CLOCK
DATA BUS
RAM/ROM
MAGNETIC

Pathlengths, Methane Percentage in Air,

and A/D Converter Errors

$\frac{\text{Methane in Air (\%)}}{\text{A/D Conversion Error (\%)}}$

Path length (cm)		100	50	10	5	3.5	2	1	.1
1/2	Methane in Air	.009†	.07†	.67	.82	.87	.92	.96	*
	A/D Error	11	1.4	.3	.5	.7	1.2	2.4	*
1	Methane in Air	.00017†	.009†	.45	.67	.76	.85	.92	.99
	A/D Error	*	11	.2	.3	.4	.6	1.2	9.8
10	Methane in Air	*	*	.0003	.018	.06	.20	.45	.92
	A/D Error	*	*	*	5.4	1.6	.5	.2	1.2

Notes: * indicates unacceptable value or uninteresting conditions.
† indicates that the transmission has been reduced by a factor of two to approximate the effects of aerosol scattering.

Table 2 presents calculations of the transmitted intensity recei by detector No. 1 for various absorption path lengths. The top value i each box of the table indicates the fraction of the incident laser beam that will be transmitted for each specific combination of path length a methane concentration. The A/D conversion error associated with the in cated laser beam attenuation is given below that value. For example, a 5% methane concentration and a 1 cm path length will yield a 67% transmission through the absorbing gas; and the error in the computed concen tration associated with A/D conversion errors is 0.3%.

To cover the entire concentration range from 100% to 0.1% with acceptable accuracy, the path length should be reduced at an intermedia concentration. The calculations presented in Table 2 suggest that a switch from 0.5 cm to 10 cm should occur at a methane concentration of approximately 3.5%. To avoid multiple insertions of the transparent ro we have chosen to establish a "dead band" for the rod motion: with the rod in place, retraction will occur when the concentration drops below with the rod retracted, insertion will occur if the concentration excee 5%. This 5:1 concentration ratio for the "dead band" will be quite

icient to avoid oscillations in the presence of the statistical concen-
ion fluctuations encountered in turbulent mixing.

In the event that the instrument will be used to measure a more ited range of concentrations, the transparent rod mechanism can be ctivated and a fixed absorption path length used. For example, Table ndicates that a 1 cm path will produce accurate concentration measure-ts (± 5%) from 40% methane to 0.2% methane. This concentration span l cover the expected concentration variations of interest at all mea-ing points except those very near the spill origin and very far downwar

The components used in the prototype have been chosen to be repre-ntative of those that would be used in producing a large number of such struments. Table 3 presents price quotations obtained from manufacture sed on the construction of 100 identical units. Many of the optical d electronic parts are relatively expensive in single quantities, but e unit costs are much less when quantity purchases are made. The total mponent cost is approximately $3,000. Our estimate of the labor costs sociated with machining, assembly, and checkout is $1,600 based on a rdened average labor rate of $20/hr. (Amortization of software develo ent is not included here; a large fraction of this task has been com-leted in the development of our prototype unit.) The total delivered ost, including manufacturer's selling expenses and profit, should be pproximately $6,000 in large (100) quantity.

. SUMMARY AND EVALUATION

We have developed an instrument to measure atmospheric methane severe environments such as large-scale LNG dispersion tests. The inst ment, based on a two-wavelength infrared He-Ne laser, is completely por able and contains internal electronics for computing methane concentra-tions and storing the resulting data in digital form. A careful analys of potential errors arising from aerosol scattering and other sources indicates that the absolute error in measured concentration will be le than 5% over the entire range of methane concentrations from 80% to 0.

Table 3

Component Cost Estimates

(Based on purchase of items for 100 instruments)

No. Per Instrument	Component	Total Price Component per Ins
1	3.39 μm He-Ne laser w/power supply	$1,000
1	Enclosure, aluminum	241
1	Cassette tape transport	325
1	Microprocessor, A/D converter, crystal clock, interface card and chips	425
1	Etalon, scanner, scanner electronics	400
3	Batteries (Gel Cell) for power	60
7	Sapphire windows, mirrors, beamsplitter	45
2	Detector and amplifier assemblies	140
1	Telemetry system (simple RC model airplane control)	60
1	Solenoid and transparent rod assemblies	40
	Miscellaneous mechanical and electrical hardware, including cabling, recharging plug, thermocouple, shock mounts, aluminum plates, and optical mounting brackets	250
	TOTAL COMPONENT COST	$2,986

Other instruments employed in previous LNG dispersion tests as catalytic sensors, grab samplers, thermal conductivity meters, a NDIR analyzers, do not possess the fast response and high intrinsic accuracy of the present instrument. Some, particularly the grab sa and catalytic sensors, are much less expensive.

Future test programs will undoubtedly use a mixture of inst ments to achieve a cost-effective balance between detailed time-res information and mean concentration measurements. The microprocesso data acquisition and storage system that we have developed should p to be a valuable prototype for use with other instruments. The con

distributed data processing and storage will become most important the number of instruments and test complexity increase.

EFERENCES

Bartz, A. M., and Ruhl, H. D. (1966), "Infrared Plant Stream nalyzers," in Applied Infrared Spectroscopy (D. N. Kendall, Ed.), einhold Publ., N. Y., pp. 398-434.

Bingham, G. E., Gillespie, C. H., and McQuaid, J. H. (1978), 'Development of a Miniature, Rapid-Response Carbon Dioxide Sensor," awrence Livermore Laboratory Report UCRL-52440, June 28, 1978.

Dewey, C. F. Jr. (1974), "Optoacoustic Spectroscopy," Optical Engineering, 13, 483.

Dewey, C. F. Jr. (1977a), unpublished estimates of turbulent mixing scales.

Dewey, C. F. Jr. (1977b), "Design of Optoacoustic Systems," Ch. 2 in Optoacoustic Spectroscopy (Y.-H. Pao, Ed.), Academic Press, N. Y., 1977.

Dewey, C. F. Jr. (1978), "Field Measurements of Atmospheric Methane with a Two-Wavelength Laser System," Abstract of paper preser at the 1978 Conference on Analytical Chemistry and Applied Spectrosc Cleveland, March 3.

Gerritsen, H. J. (1966), "Methane Detection Using a Laser," Trans. AIME, 235 (Dec.), 428-432.

Koopman, R. (1978), Lawrence Livermore Laboratory, private communication.

Moore, C. B. (1965), "Gas Laser Frequency Selection by Mole Absorption," Applied Optics, 4, 252.

Rosenberger, D. (1964), "Oscillation of Three 3P-2S Transi in a He-Ne Laser," Physics Letters, 9, 29.

Russ, R. M. Jr. (1978), "Detection of Atmospheric Methane a Two-Wavelength HeNe Laser System," M.S. Thesis, MIT.

Stein, M. I. (1978), "The Design of a Device to Measure Me Concentration," S.B. Thesis, MIT.

REPORT J

Instrumentation Assessment: JPL Laser and TBDR Methane Monitors

E. D. Hinkley

Prepared with Interagency Support for the
National Aeronautics and Space Administration
under Contract NAS-7-100

Jet Propulsion Laboratory
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FIGURES

TABLES

The Jet Propulsion Laboratory (JPL) was requested by the U. S. C
to assist in the development of advanced instrumentation for the
sensitive detection of methane gas in the vapor resulting from a
spill, and to demonstrate its operation during spill tests at Ch
Lake, California. Two types of instruments were developed: A
instrument with 0.005 second response time and 0.1% sensitivity
two-band differential radiometer (TBDR) with 0.15 second respon
and 1% sensitivity. Each of these methane-specific instruments
real-time measurements at two different locations within the va
A thermister sensor was also developed for the rapid (0.2 secor
ment of vapor temperature. Implementation of this instrumenta
Spill Tests LNG-18, LNG-19, and LNG-21 is described in this Re

Some comparisons have already been made between the JPL measur
those of other organizations involved in the China Lake test
During LNG-18, good correlation was found between the laser me
of methane and that of a nearby TSI sensor operated by the La
Livermore Laboratory (LLL). The sensitivity of the laser ins
appears to be several times better than the TSI instrument, a
comparisons should be made using data for LNG-19 and LNG-21.
in addition to methane, the vapor temperature was also measur
to be linearly related to the methane concentration over the
Quantitatively, the dependence is -2.13°C/% methane, which c
favorably with the theoretical value of -2.22°C/% methane de
Lloyd Multhauf of LLL for the conditions of LNG-18.

Laboratory research at JPL associated with this program yie
the development of a modified TBDR instrument to measure th
of oxygen in the vapor cloud, and in the development of inf
fiber optics for advanced laser detection of methane and ot
Results of this laboratory effort are also described in thi

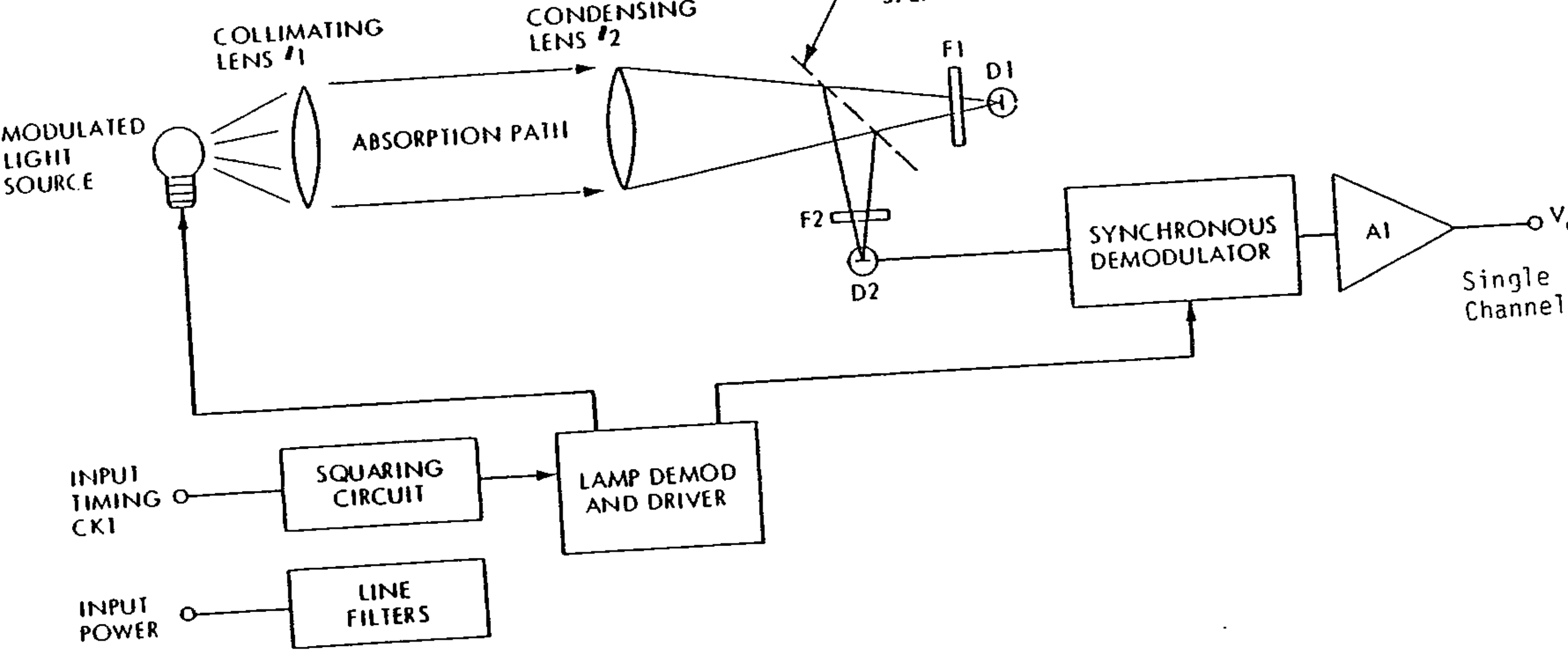
system is based upon the principle of differential absorption of radiati by methane at two narrow wavelength regions in the near infrared (2.1 an determined by filters of the broadband radiation from a thermal source. It is called the TBDR, for "two-band differential radiometer," uses a pathlength of approximately 20 cm, and is located in the midst of the vapor cloud. The second instrument is based on the very strong absorpti of laser radiation at 3.39 μm by methane, for which a pathlength of only 2 cm is adequate for the test program. These instruments are described in more detail below.

1.1 Two-Band Differential Radiometer (TBDR)

Two identical TBDR instruments were constructed during July and early August. The Block Diagram is illustrated in Figure 1. Calibration was performed on 18 August 1978 using known concentrations of methane gas contained in a 15-cm-long sample cell through which the radiation wa transmitted. These concentrations in the cell were 14.7%, 10.0%, and 5.0%, which corresponded to effective concentrations of 11.0%, 7.5%, anc 3.75% over the entire 20-cm path. A fourth sample was obtained from the natural gas system supply, and was assumed to be 97% methane, corresponc to 73% over the entire path. Table I lists the absorption measured for each of the TBDR detectors at the sample concentrations indicated:

Table I. TBDR absorption signal for various methane concentrations in a 15-cm-long calibration cell

Methane Concentration (%)	Absorption (%)
14.7	8.
10.0	5.4
5.0	2.8
97.0	40.



F1, F2: SPECTRAL FILTERS
D1, D2: DETECTORS
A1: AMPLIFIER

Figure 1. Block Diagram for TBDR Sensor Module, showing integration of optics and electronics

graphically the system response. Since the major interferant is expect to be water vapor, which absorbs equally at the center wavelengths of e filter, the differential technique is expected to reduce any potential interference from water vapor to a minimum. Verification of this did occur during the actual Spill Tests, during which both channels were monitored.

After the calibration test and check of integration with the data handl system, the TBDR units were shipped to China Lake on 16 August 1978. Checkout and connection to the Livermore system was accomplished prior the first spill test.

1.2 Laser System

The laser system developed to monitor gaseous methane during the China Lake tests is shown in Figure 3. It consists of a helium-neon laser operating at 3.39 μm, three InAs infrared detectors, a mechanical chopp and appropriate control and signal-processing electronics. The two detectors for measuring methane are located 1.5 and 2.5 meters above the ground. The upper one is designated "Sensor #1"; the lower one, "Senso #2." A third detector is used to monitor the laser power in order to e that any "signals" are not caused by laser power variations.

An air-temperature measuring thermister is located between Sensor #1 an Sensor #2. Three other thermisters are located near the three infrared tectors (two detectors for the methane measurements; the third for lase power). Thermisters to measure temperatures near the infrared detector were deemed necessary in order to maintain a check on the system under rigors of the hot desert environment. (They turned out to be unnecessa cause the heat capacity of the detector holders kept the temperature re ly constant.) An air conditioner is used prior to the test to maintair suitable temperature. The interior of the laser system is shown in F which illustrates location of the important elements.

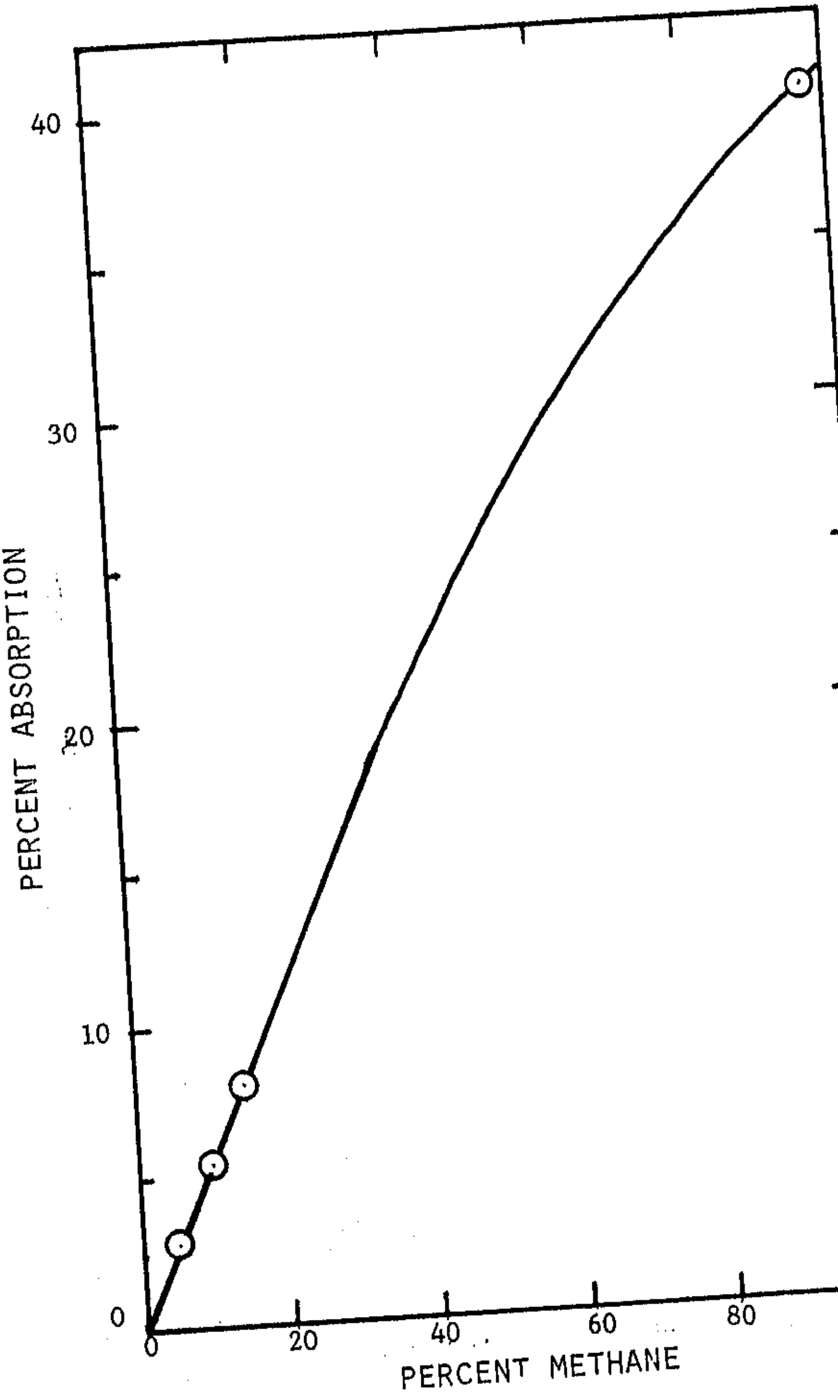
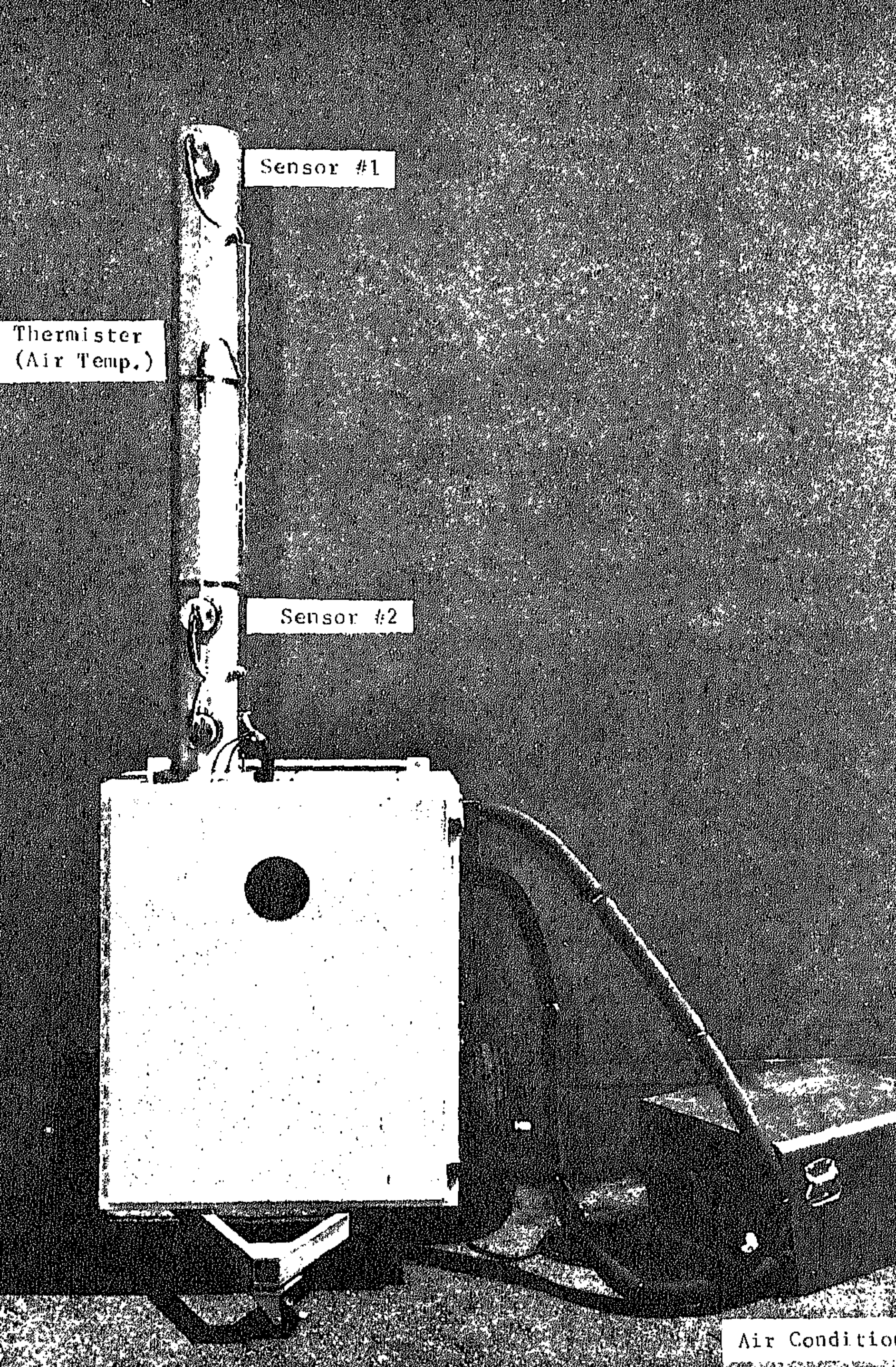
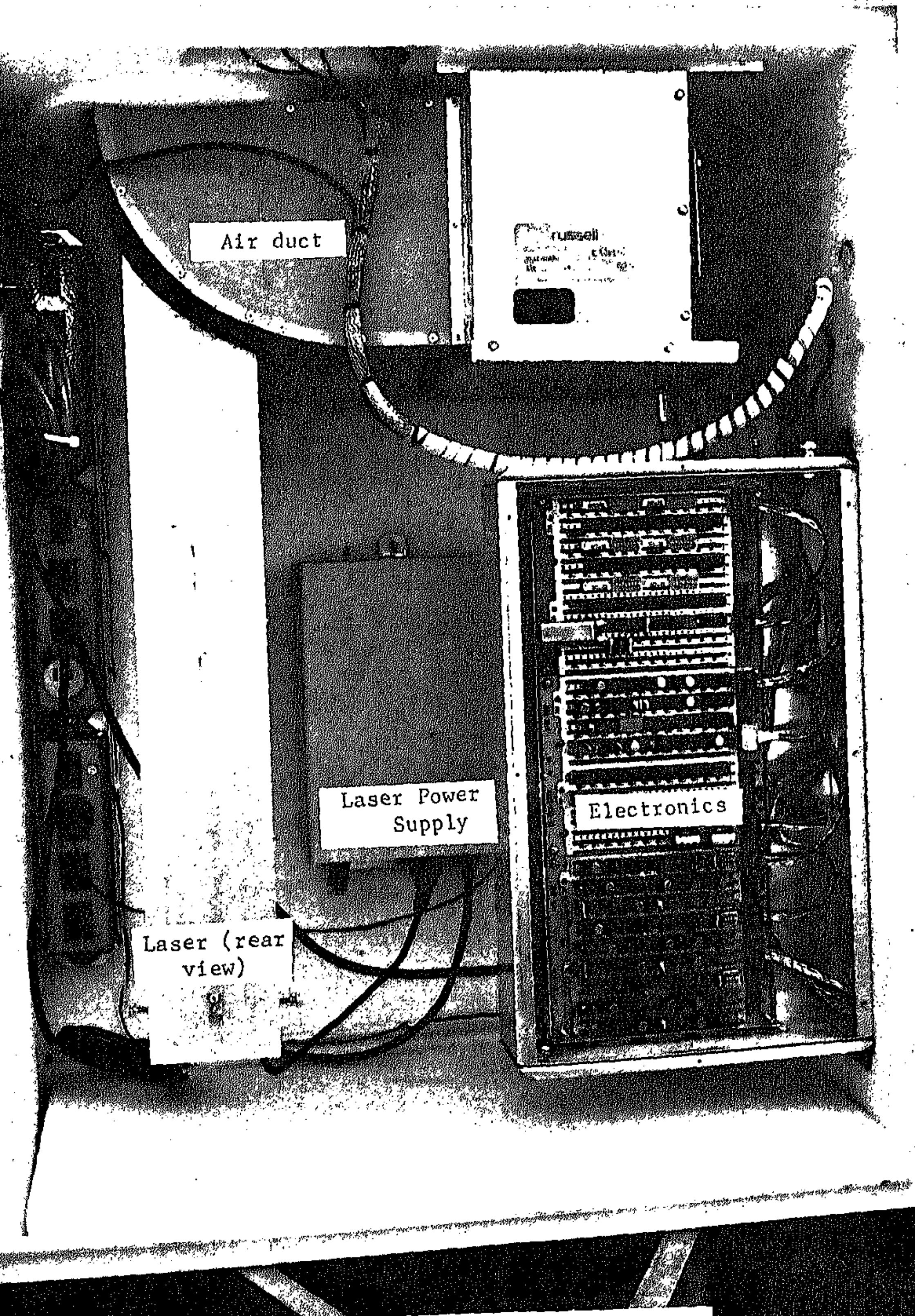


Figure 2. TBDR System response to various methane



Sensor #1
Thermister
(Air Temp.)
Sensor #2
Air Conditio


Air duct
Laser Power Supply
Electronics
Laser (rear view)

1.2.1 Linearity Test of InAs Detectors

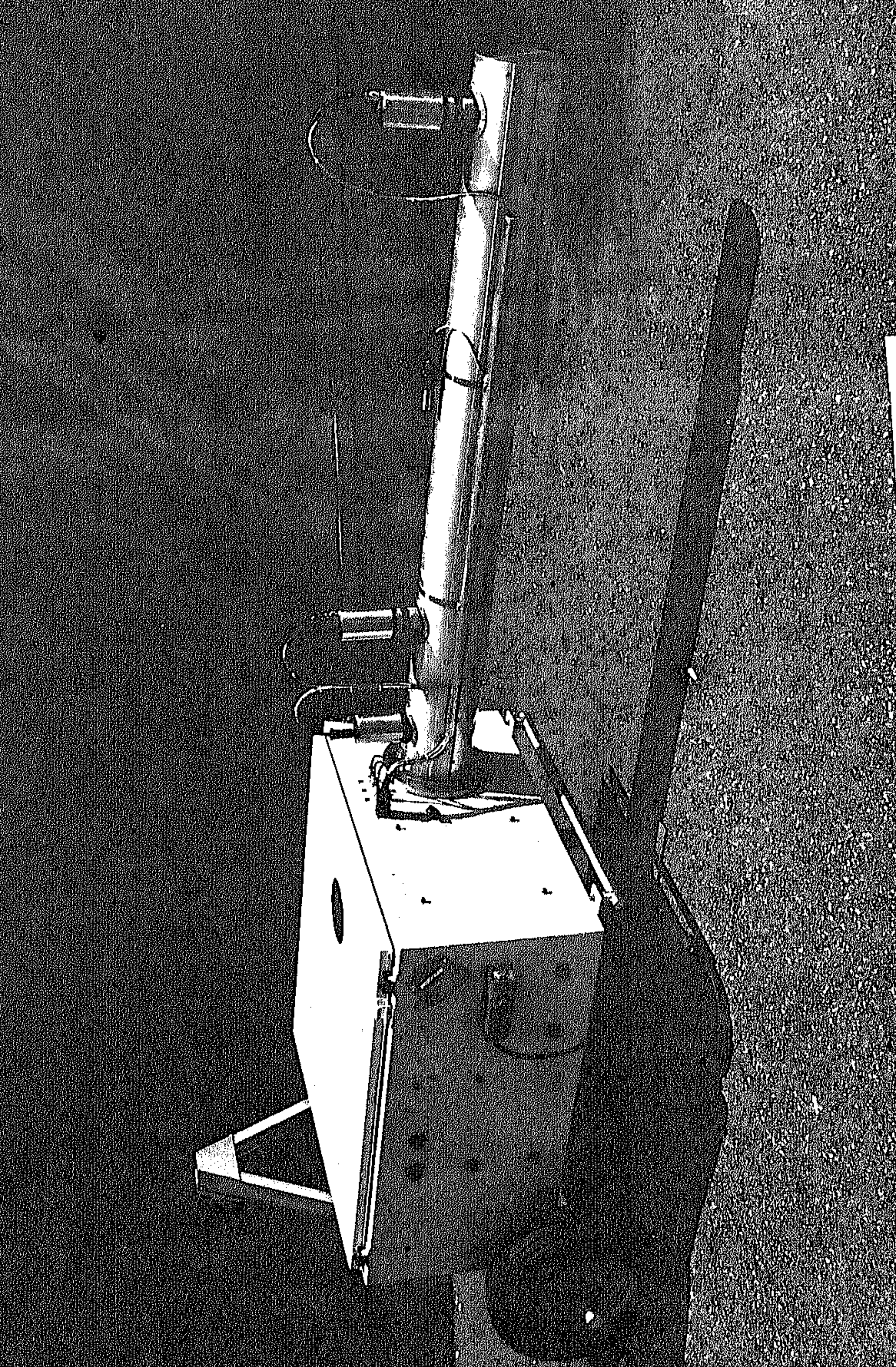
In order to ensure that the laser system will operate within the linear r of the infrared detectors, a linearity check was made by observing the ab sorbance of a plastic sheet (Saran Wrap) inserted into the laser beam und different conditions of total power impinging on the detector. Results c this test are shown in Figure 6, where the ordinate denotes the absorbanc and the abscissa the detector voltage. Since the absorbance remains con- stant to approximately 6 mV on the detector, the voltages of the laser sy tem detectors are kept below this value. Linearity is confirmed by usinc sample cells containing a variety of methane concentrations. Finally, if the ultimate detector noise limit using a 0.01 second integration time is 6×10^{-9} V, the available dynamic range is 10^6.

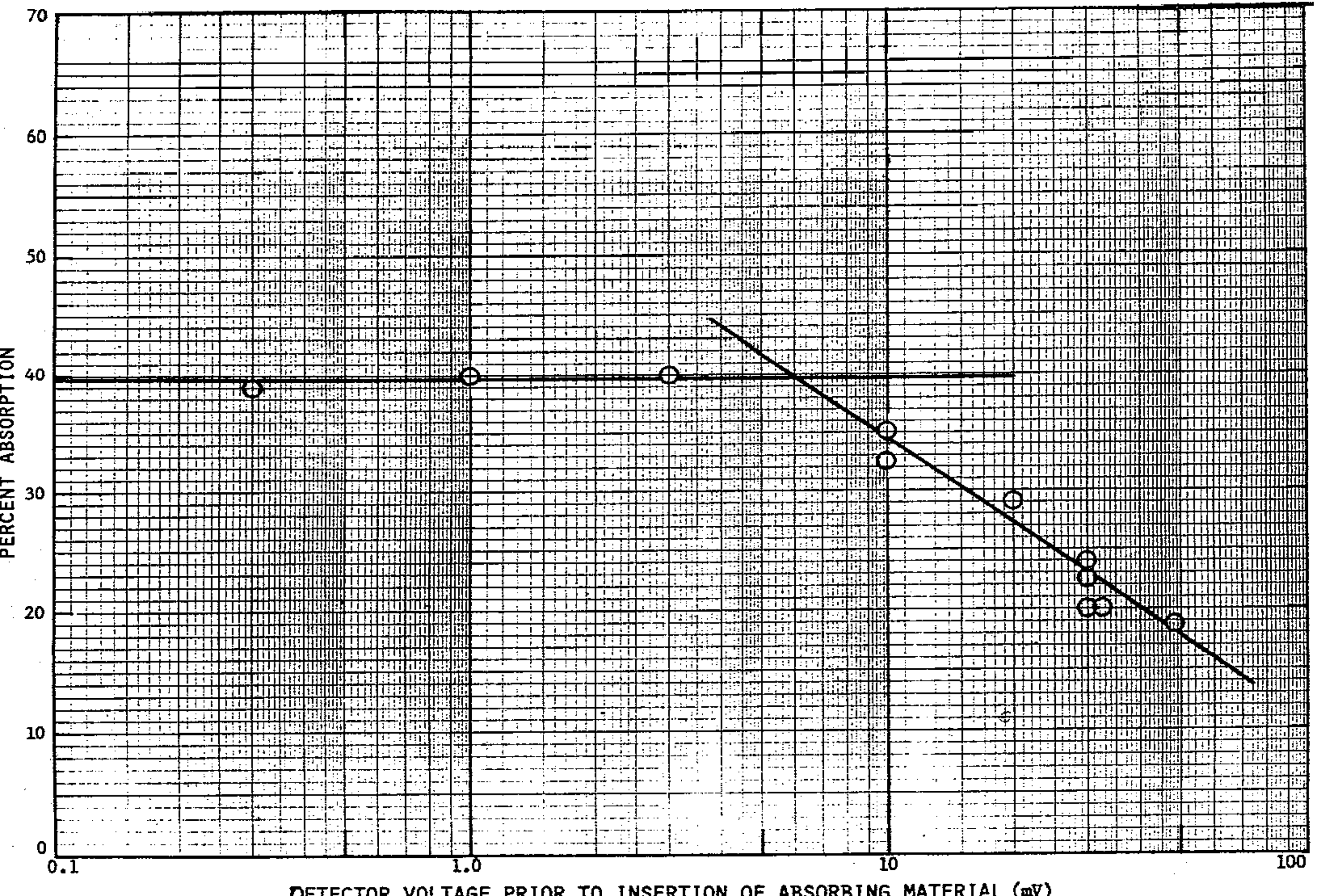
1.2.2 Performance Test at JPL

The laser system was tested on 15 August 1978 for response to various cor centrations of methane in a 1-cm-long calibration cell. The detector voltage was amplified and measured by an analog strip-chart recorder as well as a digital voltmeter. Figure 7 shows a strip-chart record of the calibration signals. The digital data are shown in Table II below.

Table II. Amplified detector voltage corresponding to various methane concentrations in a 1-cm-long cell.

	Sensor Voltages (V)	
Absorber	Sensor #1	Sensor #2
No Cell	4.50	3.85
Cell, 0% CH_4	3.47	3.05
5% CH_4	1.46	0.98
14.7% CH_4	-0.660	-0.83
100% CH_4	-2.497	-2.498
Blocked	-2.499	-2.500




PERCENT ABSORPTION
70
60
50
40
30
20
10
0
0.1
1.0
10
100
DETECTOR VOLTAGE PRIOR TO INSERTION OF ABSORBING MATERIAL (mV)

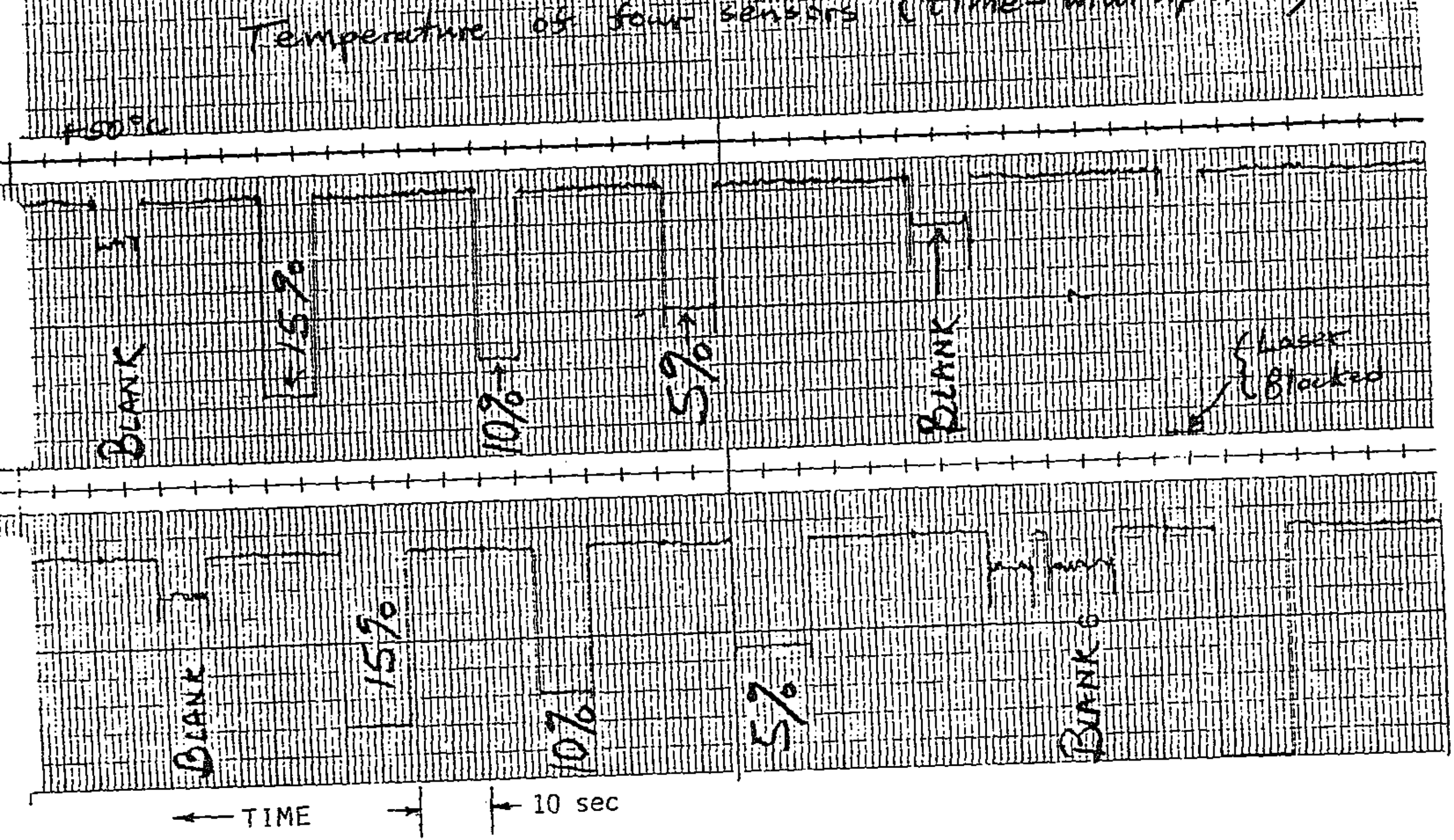


Figure 7. Calibration test of laser system for methane detection

1.2.3. Shipment to China Lake

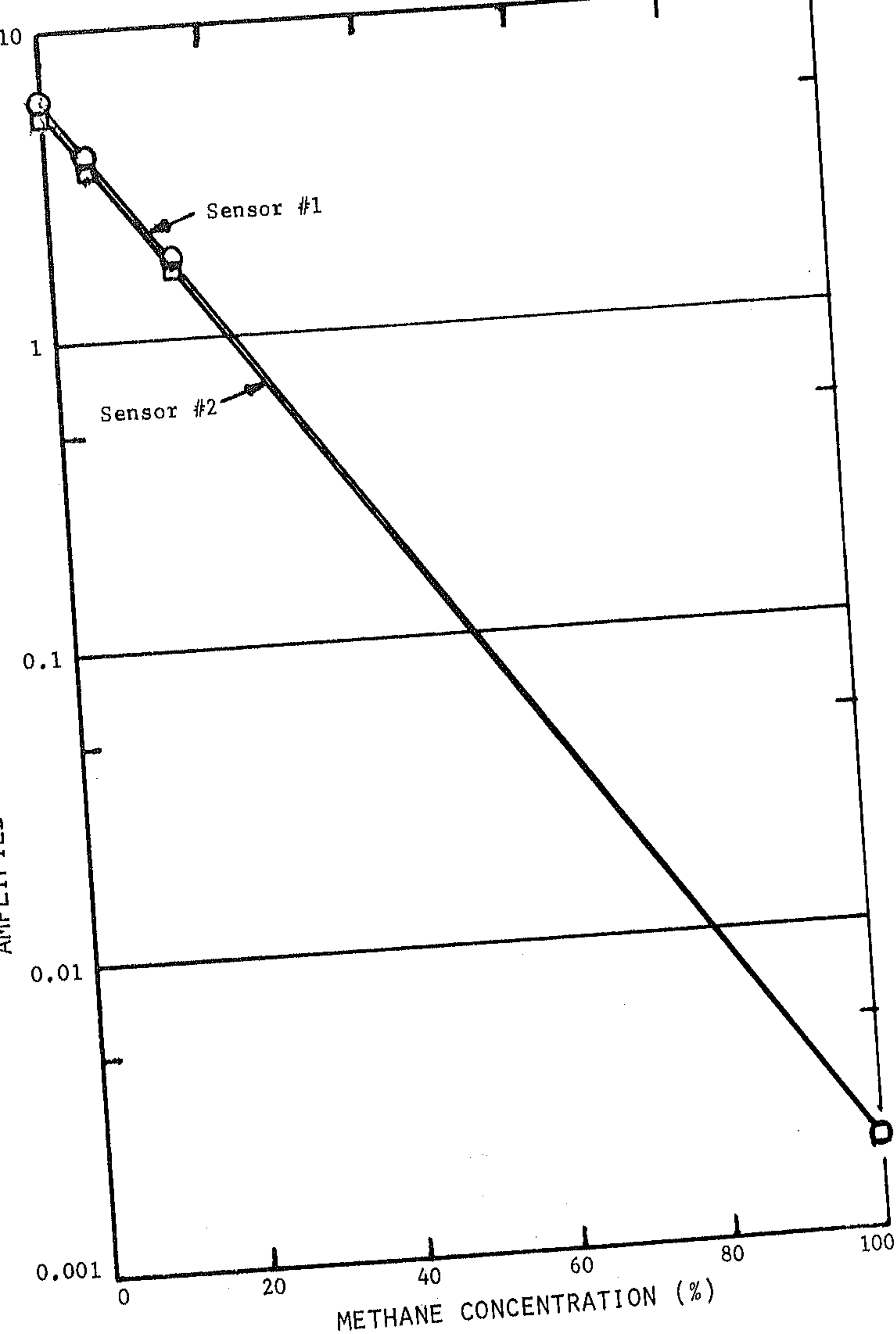
The laser system was shipped to China Lake on 18 August 1978. with the electronics systems in the Livermore trailer, and syst were performed during the following week. The laser system inco four data recording systems:

1) Six-channel analog recorder (which operates at 2.5 c during spill test) at the spill test location. The channels are: Sensor #1; amplified Sensor #1 for hi methane concentrations; Sensor #2; amplified Sensor laser power; system temperatures (four temperatures, multiplexed).

2) Six-channel analog recorder at the Livermore trailer record the same data as above, but with the capabili replace the two amplified sensor channels with logar converted channels so that the methane concentration be linear with recorder divisions.

3) A JPL magnetic tape recorder, which records the abov together with the TBDR data and time information, at voltages have been converted to frequencies via volt frequency converters at the spill site. This tape c be replayed in any desired format.

4) Magnetic tape recorder operated and owned by Lawrenc Livermore Laboratory, which records the above data t with those from the Livermore and USCG instruments. of this tape is to permit the development and evalua mathematical models for the vapor clouds.



f laser system sensors to various methane concentra
easurements)

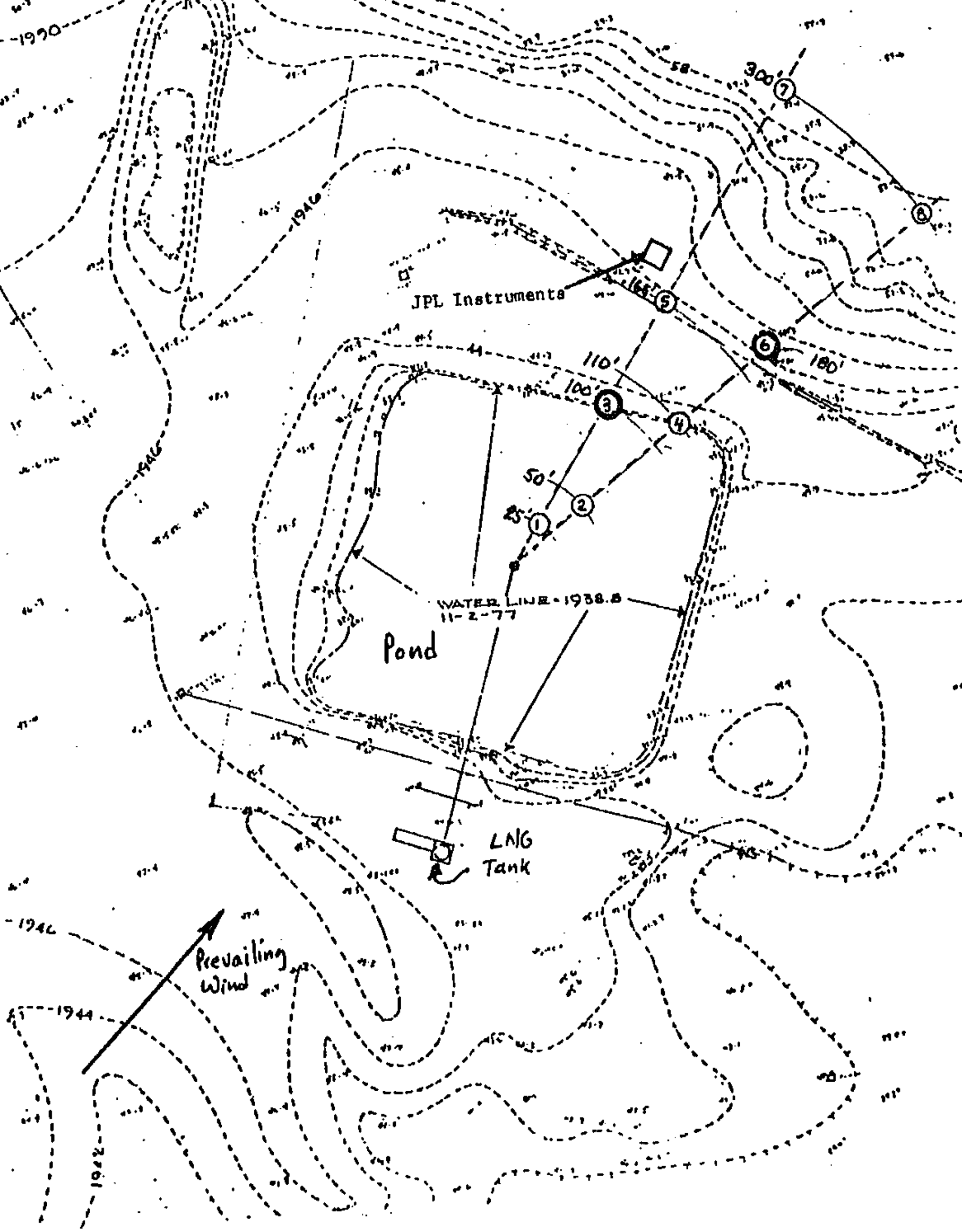
. LNG Spill Tests at China

uring the period from 31 August 1978 to 20 November 1978, four LNG spills ere made at China Lake, California. These are designated LNG-18 (8/31/78) NG-19 (9/13/78), LNG-20 (11/9/78), and LNG-21 (11/20/78). During LNG-20 n abrupt change in wind direction during spill caused the vapor cloud to ompletely miss the JPL instrumentation; consequently, no data from LNG-20 re presented in this Report. Spill tests LNG-18 and LNG-21 produced seful data for a relatively long period of time (more than one minute) ecause of favorable wind conditions. For LNG-18, comparison is made betwee the JPL measurements and those obtained from another methane sensor operate y LLL. For LNG-21, it has been possible to directly compare the laser sens easurement, TBDR measurement, and air temperature. Although the data for NG-19 were sparse due to the adverse change in wind direction mentioned above, useful data were obtained by both the laser and TBDR instruments. I particular, the detection of "signals" on both "signal" and "reference" channels of the TBDR underscored the need for a reference channel, and indicate the apparent presence of ice crystals during a portion of the test. The su tions which follow describe in detail results of the three useful spill tes

Figure 9 is a photograph of the JPL instrumentation on location at China Lake. On the left are shown two TBDR sensors on a tripod mount at an elevation of 0.5 meters. The horizontal paths were 20 cm for most tests. The laser system was located slightly to the right of the TBDR sensors, and the engineer is seen in Fig. 9 adjusting the lower sensor (Sensor #2) which is 1.5 meters above the ground. The upper sensor (Sensor #1) is 2.5 meters above the ground. The white box on the extreme right houses the field multi-channel recorder. Sensors of other investigators are visible i the background.

Figure 10 shows the location of the JPL instrumentation relative to the lake and spill point. The equipment is 55 meters from the spill point, and 3 meters northwest of a line corresponding to the (historically) average wind direction (see Fig. 11).


LASER SYSTEM
RECORDER
SIGNAL ENCODER
TBDR
TBDR



ure 11. Contour plot of LNG Spill Test Site, indicating location of JP instrumentation. (from R. Koopman, LLL)

data. Four thermisters were used, to provide indications of temperature of the three InAs detectors as well as the air temperature. Time-divisi multiplex was used to record the temperature data on a single channel. LNG-18 was the first spill test involving this instrumentation, and it turned out that the scales for the strip-chart record of the TBDR and temperature data were set to cover too wide a range, resulting in rather limited signal excursions for some of the real-time data. However, sinc all of the data were recorded on magnetic tape, they can be displayed wi full system sensitivity, if desired. For this present Report, the data were from the strip-charts. Spill occurred at 14:56:30 on 8/31/78, and lasted for 67 seconds. Spill volume was 4.39 m^3 of LNG.

2.1.1 Instrument Location and Test Conditions

The two TBDR sensors and the laser system were located as described ear approximately 55 meters from the spill point. The ambient temperature 36°C (97°F), and the wind was gusty to 15 knots (7.7 meters/sec.).

2.1.2 LNG Vapor Clouds

Two distinct vapor clouds were detected during LNG-18, as illustrated i Fig. 12. The first cloud reached the JPL instruments 40.2 seconds afte spill valve was opened; the second arrived 61.4 seconds after spill. Duration of the first cloud was 2.4 seconds at Sensor #1 (2.5 meters ab the ground) of the laser system, and 4.6 seconds at Sensor #2 (1.5 mete above the ground). Duration of the second (main) cloud was 39.4 second at Sensor #1, and 41.0 seconds at Sensor #2. A time-expanded record of the laser data is shown in Fig. 13 (a-c). The laser power was also mon by a third InAs detector, and was found to be essentially unchanged dur the test period. Four temperatures were also measured, as shown, but t range selected a-priori was too broad to provide meaningful data from t strip-chart.

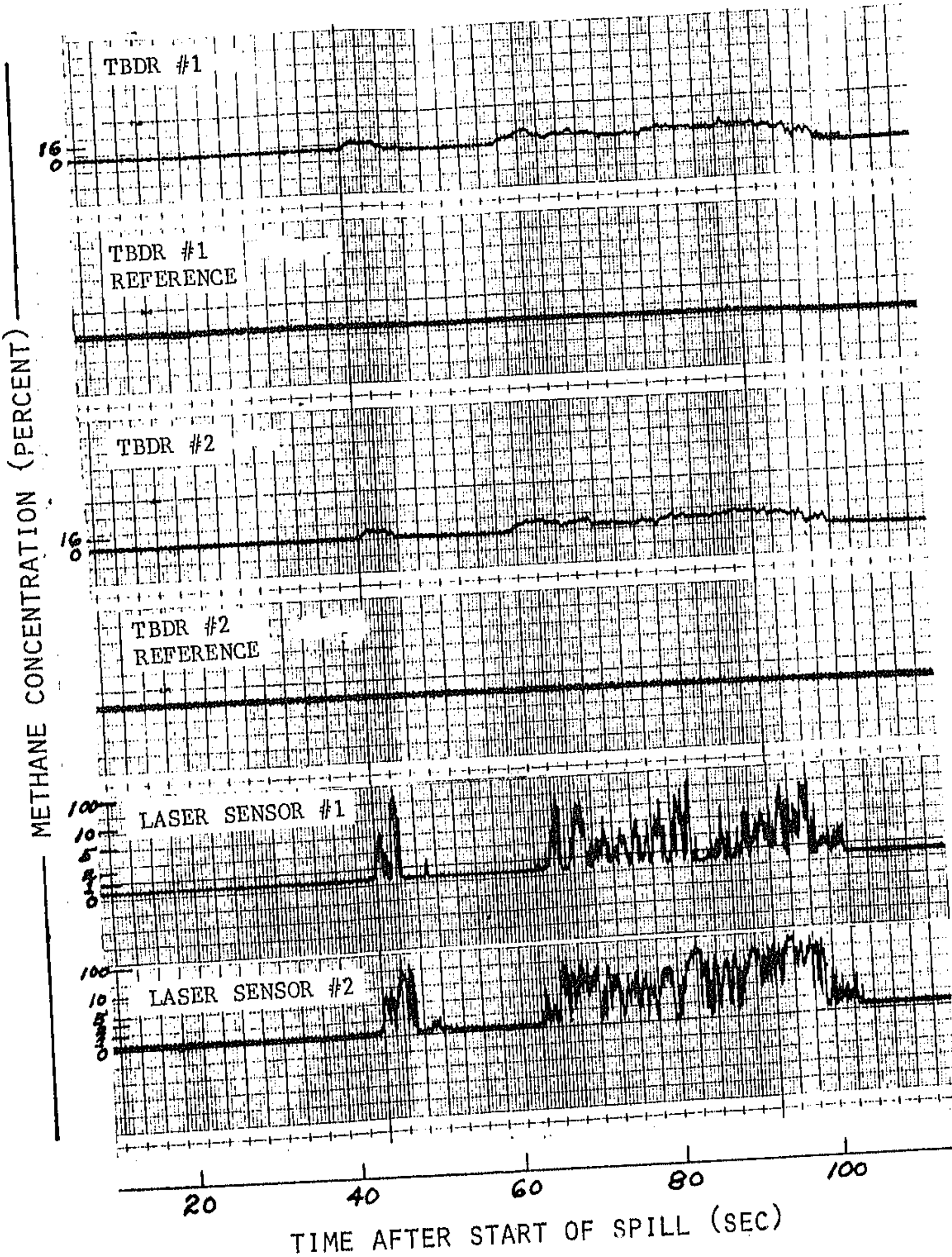
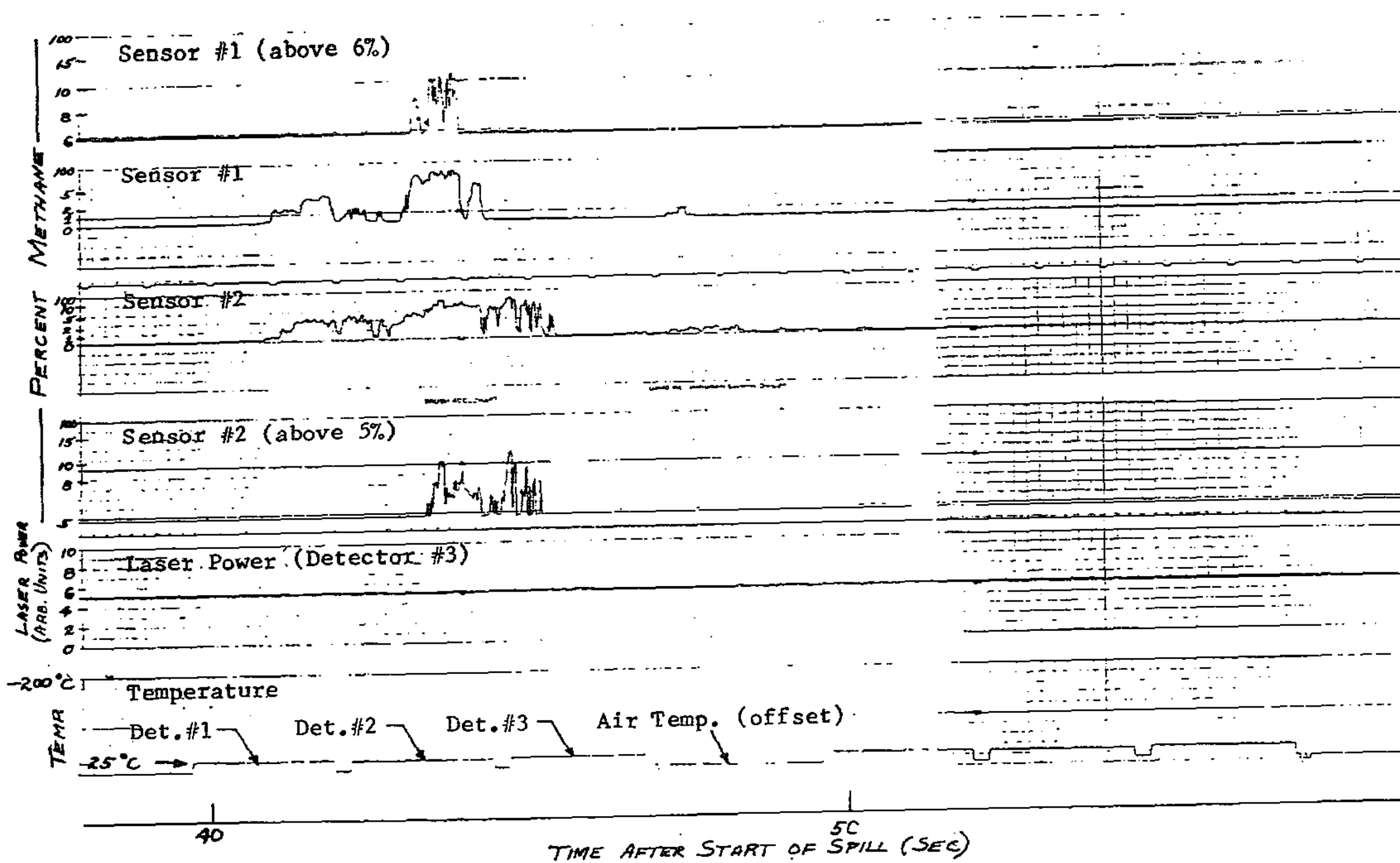


Figure 12. JPL sensor measurements of methane during LNG-18 Spill



Sensor #1 (above 6%)
Sensor #1
Sensor #2
Sensor #2 (above 5%)
Laser Power (Detector #3)
Temperature
Det. #1
Det. #2
Det. #3
Air Temp. (offset)
METHANE PERCENT
LASER POWER (ARB. UNITS)
TEMP
-200°C
25°C
40
5C
TIME AFTER START OF SPILL (SEC)

Fig. 13(a)

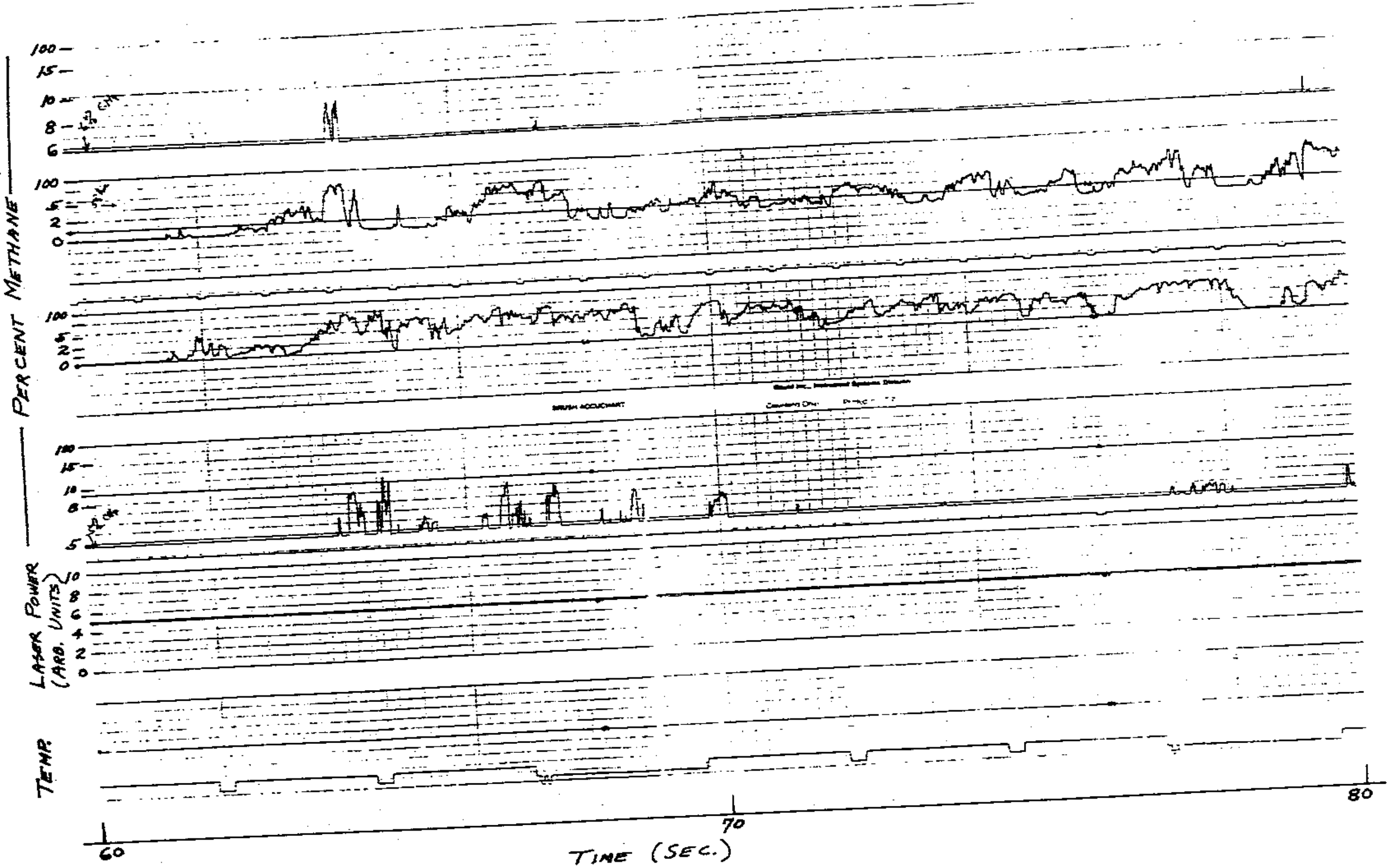
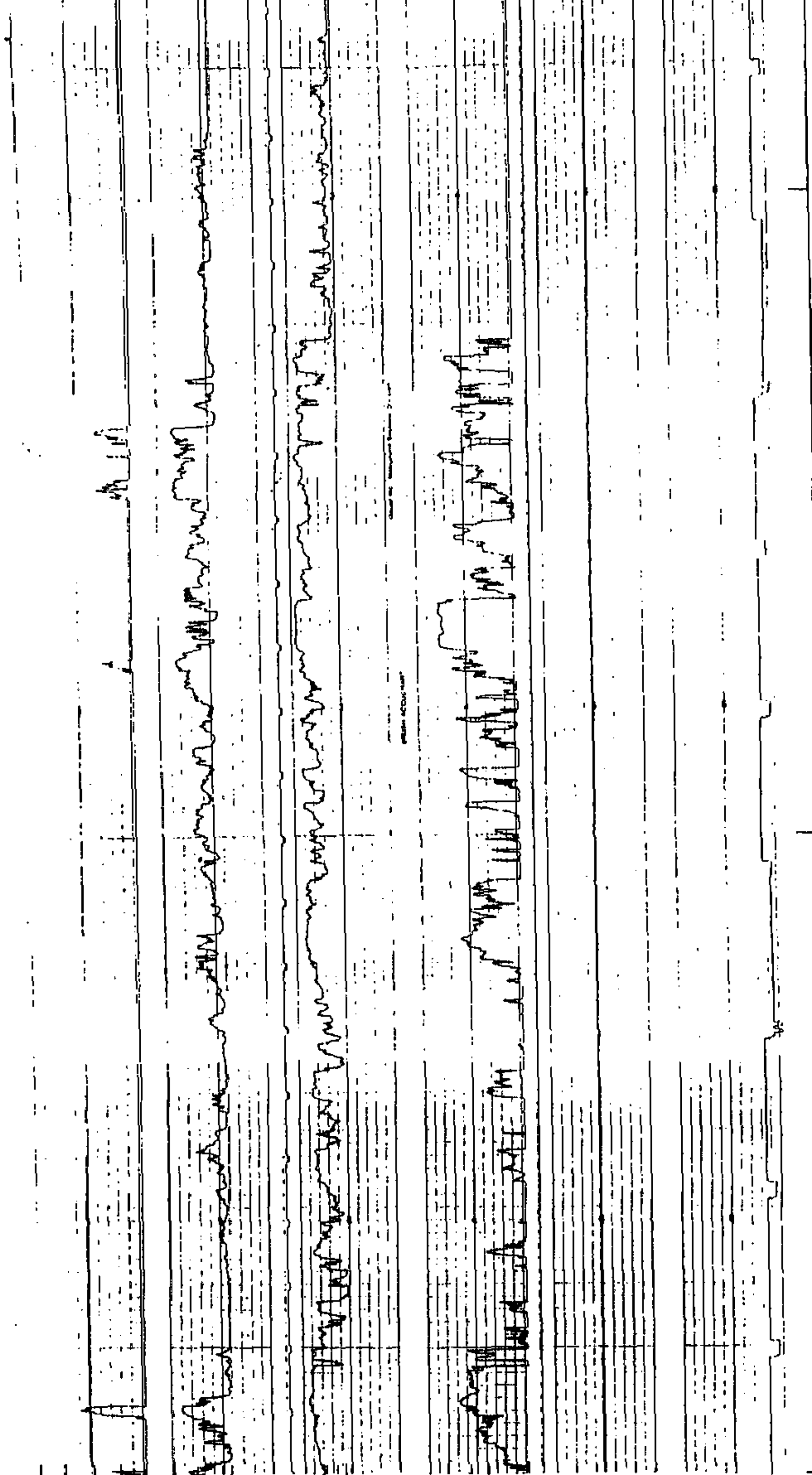

PERCENT METHANE
LASER POWER (ARB. UNITS)
TEMP.
TIME (SEC.)
60
70
80
BRUSH ACCUCHART

Figure 12(b)



maximum methane concentration in the first cloud was 11.1% at Sensor #
10.9% at Sensor #2. The maximum methane concentration in the second
oud was 11.4% at Sensor #1, and 14.2% at Sensor #2. These occurred at
nes of 80.8 seconds and 93.4 seconds, respectively, after the spill
lve was opened. As expected, these values are somewhat lower than thos
asured by the TBDR instrument, which is located closer to the ground
ere the cooler, heavier gas is expected to be. The TBDR data did not
hibit the expected rapid time of response (0.15 seconds); presumably,
is is due to path-averaging over the 20-cm optical path, which is not
pronounced in the 2-cm path of the laser system.

.1.3 Time Above 5% Methane

ince methane gas can be explosive in the 5-15% concentration range, it
ay be useful to know the extent of time the 5% value was exceeded in
oth of the observed vapor clouds:

First Cloud: Sensor #1 (h = 2.5 meters) showed that the methane concentration was above 5% for 0.89 ± 0.01 seconds, or 26% of the duration of the first cloud. Sensor #2 (h = 1.5 meters) showed that the 5% value was exceeded for 1.40 ± 0.01 seconds, or 30% of the total time th cloud was present.

Second (Main) Cloud: Sensor #1 indicated that the 5% value was exceeded for 2.5 ± 0.1 seconds, or 6.3% of the second cloud's duration whereas Sensor #2 yielded corresponding values of 14.5 ± 0.1 seconds and 35%.

2.1.4 Discussion of LNG-18

In addition to providing numerical data on the vapor clouds of LNG-18
a comparison was made between the methane measurements of Sensor #2 a
TSI data recorded at 1-m elevation by LLL at Station 6, located 24 me
away, but the same distance from the spill point (see Figure 11). Fi
14 illustrates a surprisingly good correlation between the TSI and la
measurements in concentration and time. This suggests that both ins
... are calibrated properly.

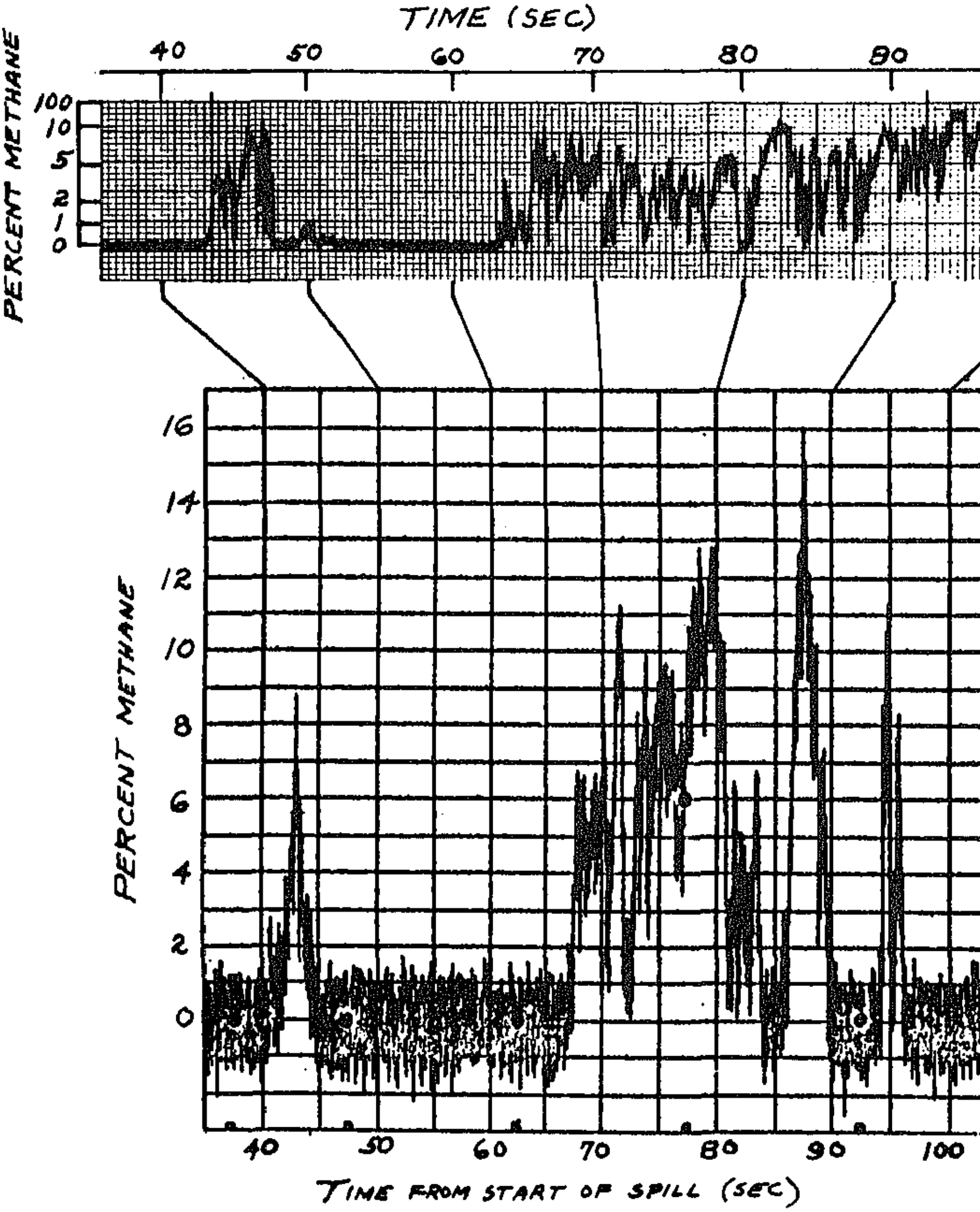


Figure 14. Metnane concentration measurements for LNG-18 Spill Te
from (a) Lawrence Livermore Laboratory TSI sensor at S
(From R. Koopman, Memorandum of 10/30/78, Fig. 9) and
JPL Laser Sensor #2.

LNG-19 (9/13/78)

rder to accommodate a Raman lidar system for one spill test, LNG-19 performed in the darkness of early evening, at 7:30 p.m. The spill ed for 63 seconds, with both TBDR units and both laser sensors ational.

.1 Instrument Location and Test Conditions

instrument locations for LNG-19 were the same as for LNG-18, roximately 55 meters from the spill point. At the time of the spill, wind direction shifted from SW to WSW, with the result that most of vapor cloud missed the JPL instrumentation. Useful data were obtaine ever, and are presented below. Wind speed was 15-20 knots.

2.2 LNG Vapor Clouds

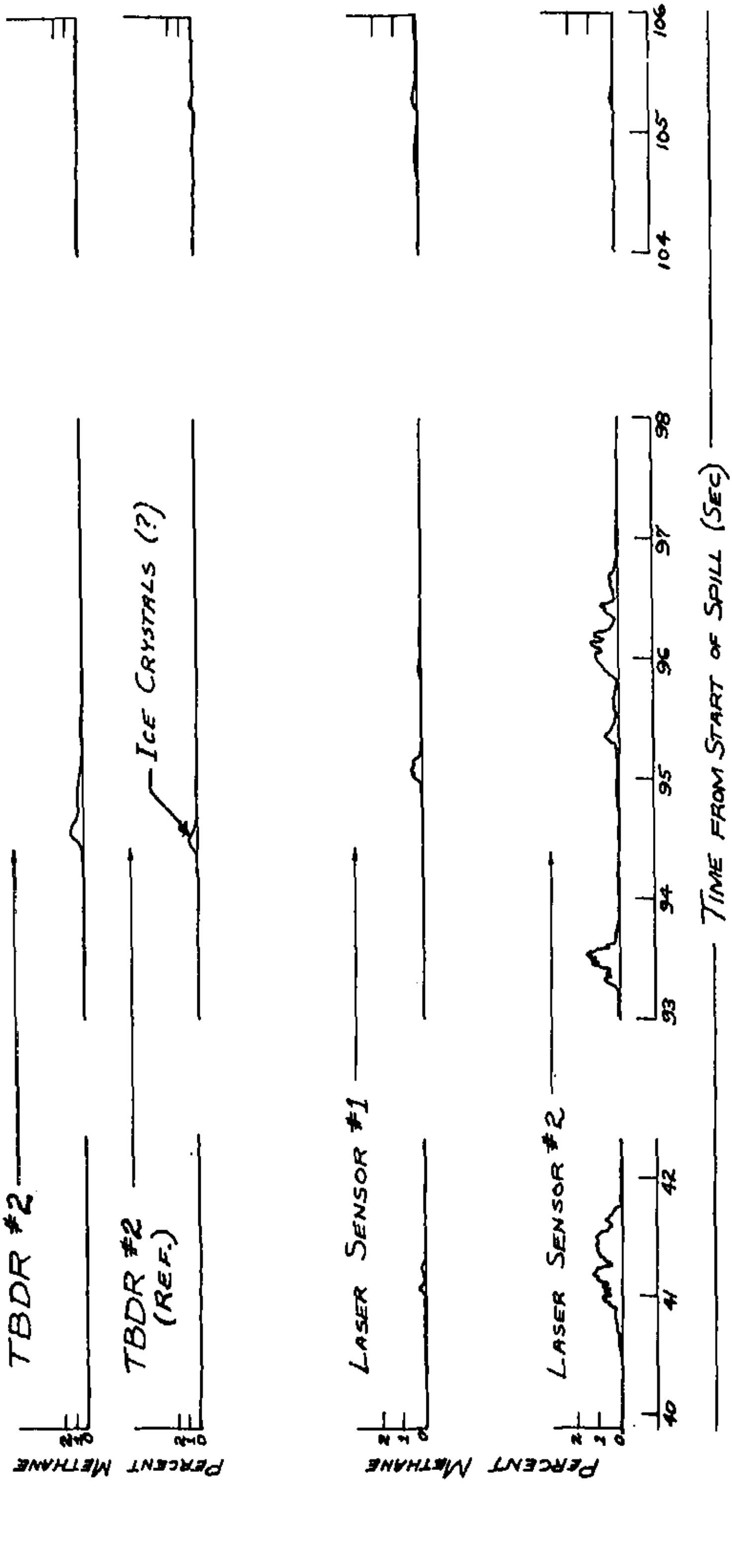
gure 15 illustrates the methane concentration data obtained by one of e TBDR units (the other did not exhibit any signal change) and the two ser sensors. Several small puffs were observed. The first puff occur 40.4 seconds after start of spill, lasted for 1.0 second at Laser Sen , and 1.5 seconds at Laser Sensor #2. Peak concentrations were 0.28% d 1.28%, respectively.

he second puff occurred at 95.0 seconds at Sensor #1, and 93.2 seconds t Sensor #2, lasting for 1.0 second and 3.8 seconds, respectively, with eak concentrations of 0.44% and 1.46%.

The third puff occurred at 105.2 seconds at Sensor #1, lasting for 0.28 seconds. That same puff lasted for 0.12 seconds at Sensor #2. The pea concentrations were 0.14% and 0.12% for Sensors #1 and #2, respectively

2.2.3 Discussion of LNG-19

Although the bulk of the vapor from Spill Test LNG-19 missed the JPL i mentation, several small puffs of methane-laden vapor were detected an quantified. The maximum recorded concentration was 1.28% methane. Fi 15 shows interference in the reference channel of the TBDR unit, sugge


TBDR #2
TBDR #2
(REF.)
ICE CRYSTALS (?)
LASER SENSOR #1
LASER SENSOR #2
PERCENT METHANE
PERCENT METHANE
2 1 0
2 1 0
2 1 0
2 1 0
40
41
42
93
94
95
96
97
98
104
105
106
TIME FROM START OF SPILL (SEC)

.3 LNG-21 (11/20/78)

or this spill test, the last in the current series, both laser sensors, ne TBDR sensor, and the thermister for measuring air temperature were perational. (The other TBDR unit had been returned to the laboratory or further studies.) Spill occurred at 3:10 p.m, and lasted for pproximately 58 seconds.

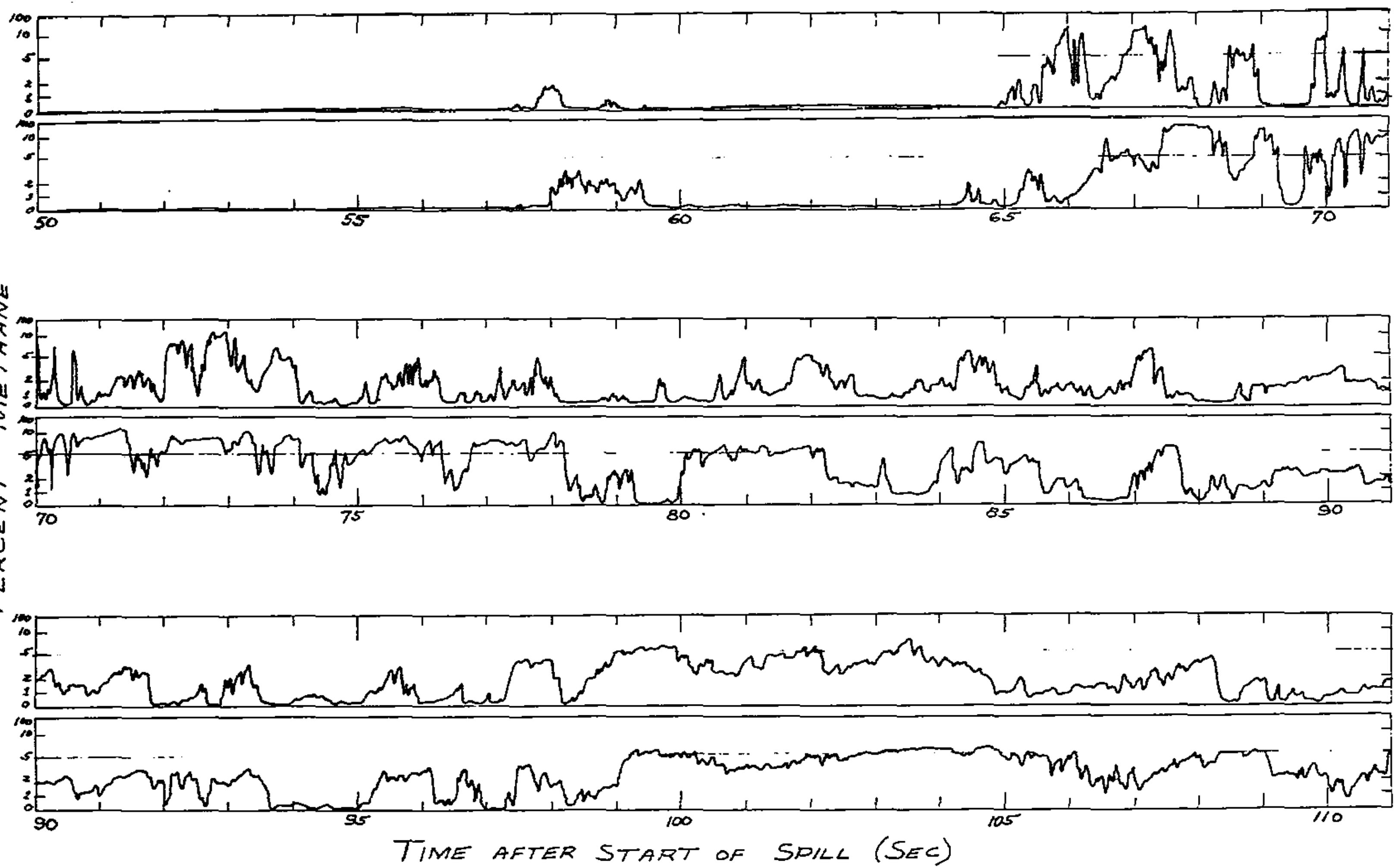
2.3.1 Instrument Location and Test Conditions

The location of the JPL instruments remained the same as for the earlier tests, but only one TBDR unit was used, and it was situated very near (within 20 cm) the Laser Sensor #2 in order to obtain correlative measu ments. The air-temperature-measuring thermister was moved down the las instrument column to within a few cm of Sensor #2 also, and the time-division multiplex circuit was modified so that a continuous measuremen of air temperature could be recorded during the test. Laser Sensor #2 provided data 2.5 meters above the ground, as before.

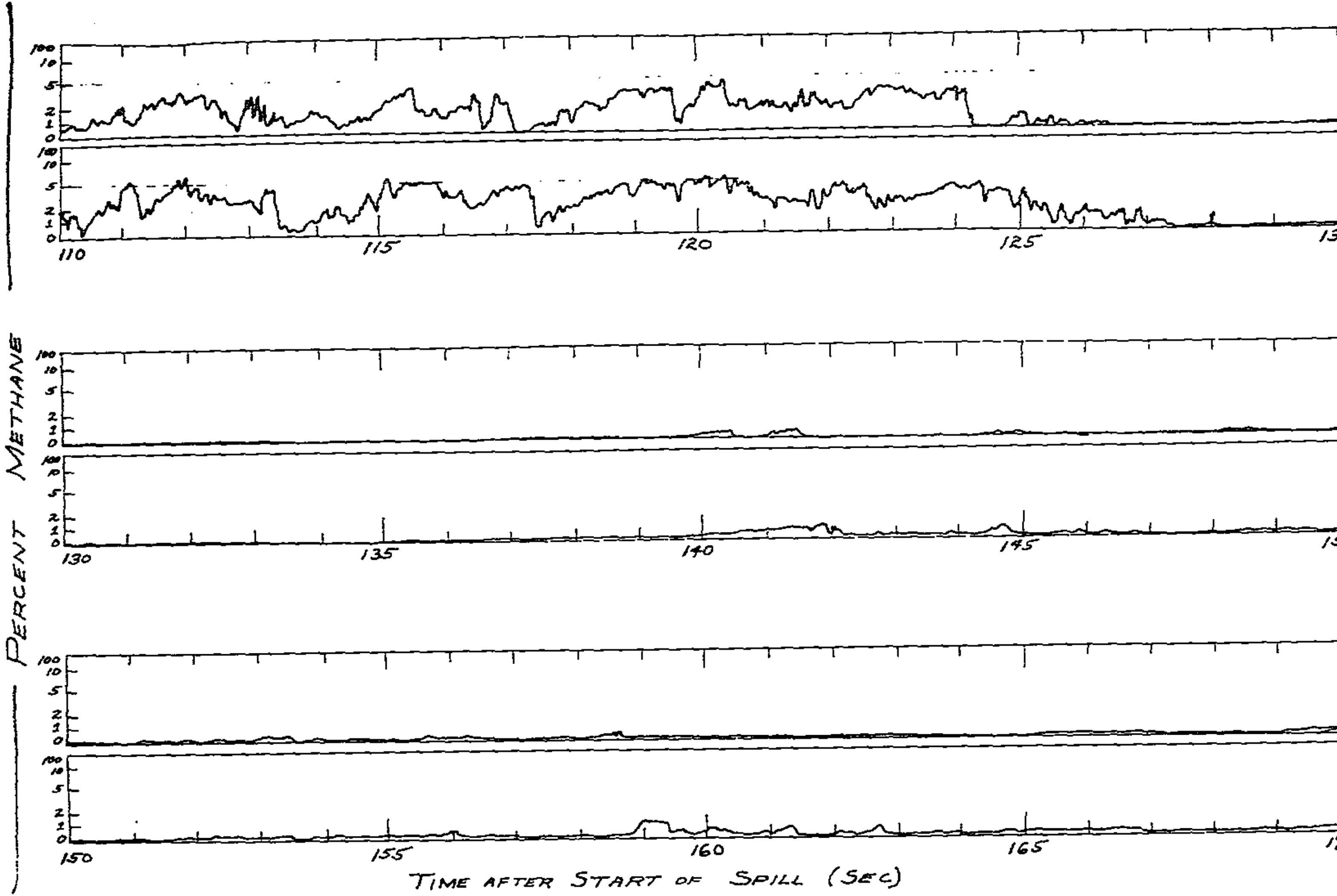
The wind direction before the spill was from the SW, averaging 5-10 kno At time zero it shifted toward the SSW, and one minute later back towa the SW. The effect of this on the JPL measurements was that no indica of methane was observed until nearly one minute after spill, at which the change in wind direction brought the main cloud in the vicinity of instruments.

2.3.2 LNG Vapor Clouds

The JPL instruments recorded over 70 seconds of continuous data. Fig 16 (a-b) shows the laser data, illustrating two puffs of methane-lade vapor. The first puff occurred at 57.2 seconds after spill, and last for 0.3 seconds at Sensor #1 and 1.5 seconds at Sensor #2. Peak conc were 1.8% and 3.8%, respectively. The main cloud occurred at 64.2 se and lasted for 61.7 seconds at Sensor #1, and 63.2 seconds at Sensor Peak concentrations were 11.9% and 13.5%, respectively, at the two se locations.



PERCENT METHANE
50
55
60
65
70
75
80
85
90
95
100
105
110
TIME AFTER START OF SPILL (SEC)



PERCENT METHANE
100
10
5
2
1
0
110
115
120
125
130
135
140
145
150
155
160
165
TIME AFTER START OF SPILL (SEC)

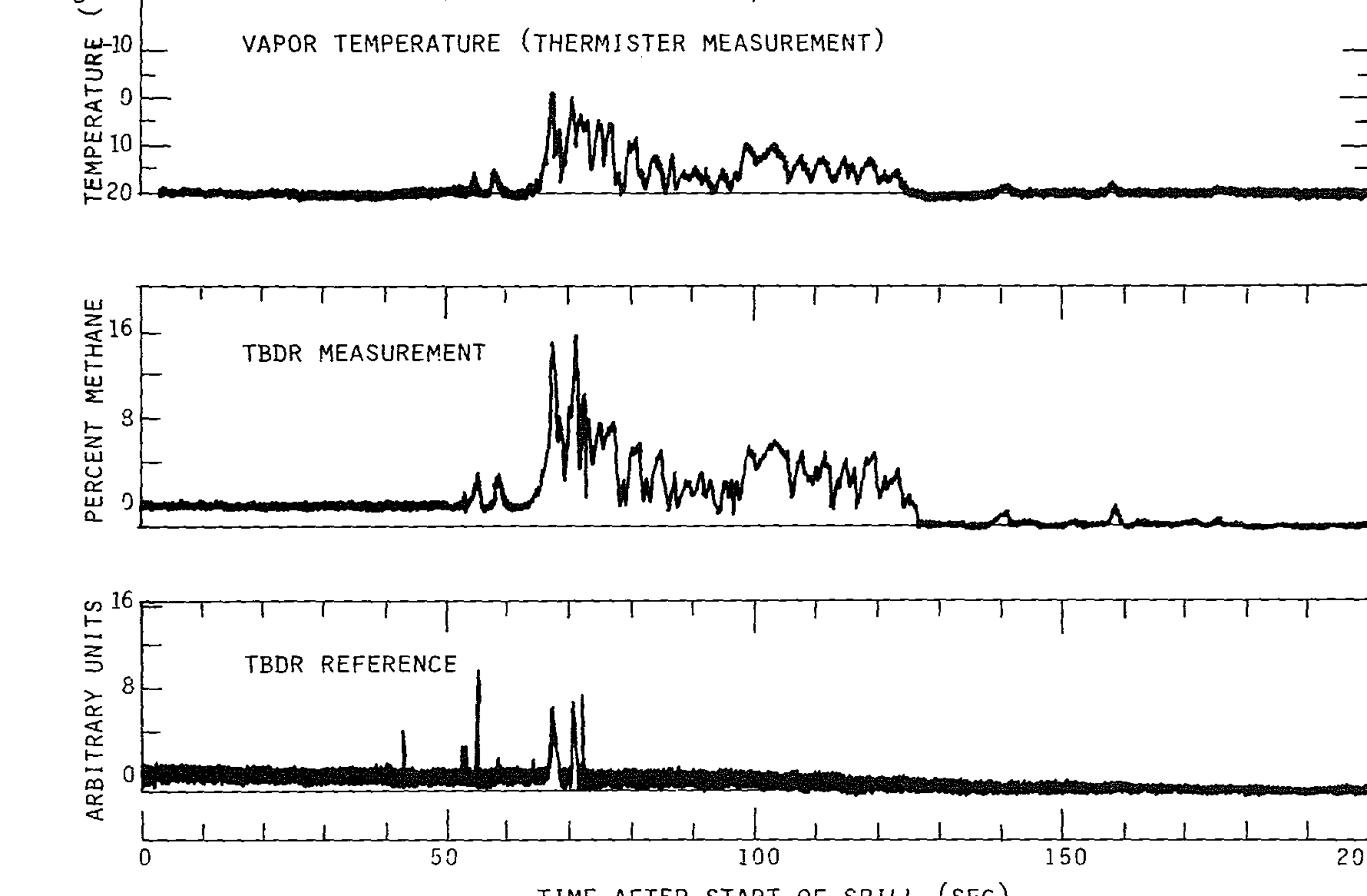
order to determine the fraction of time the methane concentration exceeded 5%. For the first puff, as indicated earlier, the concentration never exceeded 1.8% at Sensor #1 and 3.8% at Sensor #2. For the main vapor cloud the methane concentration exceeded 5% for 8% of the time at Sensor #1, and for 27% of the time at Sensor #2. These numbers should be compar with 6.3% and 35%, respectively, for LNG-18.

2.3.4 Air Temperature Measurement

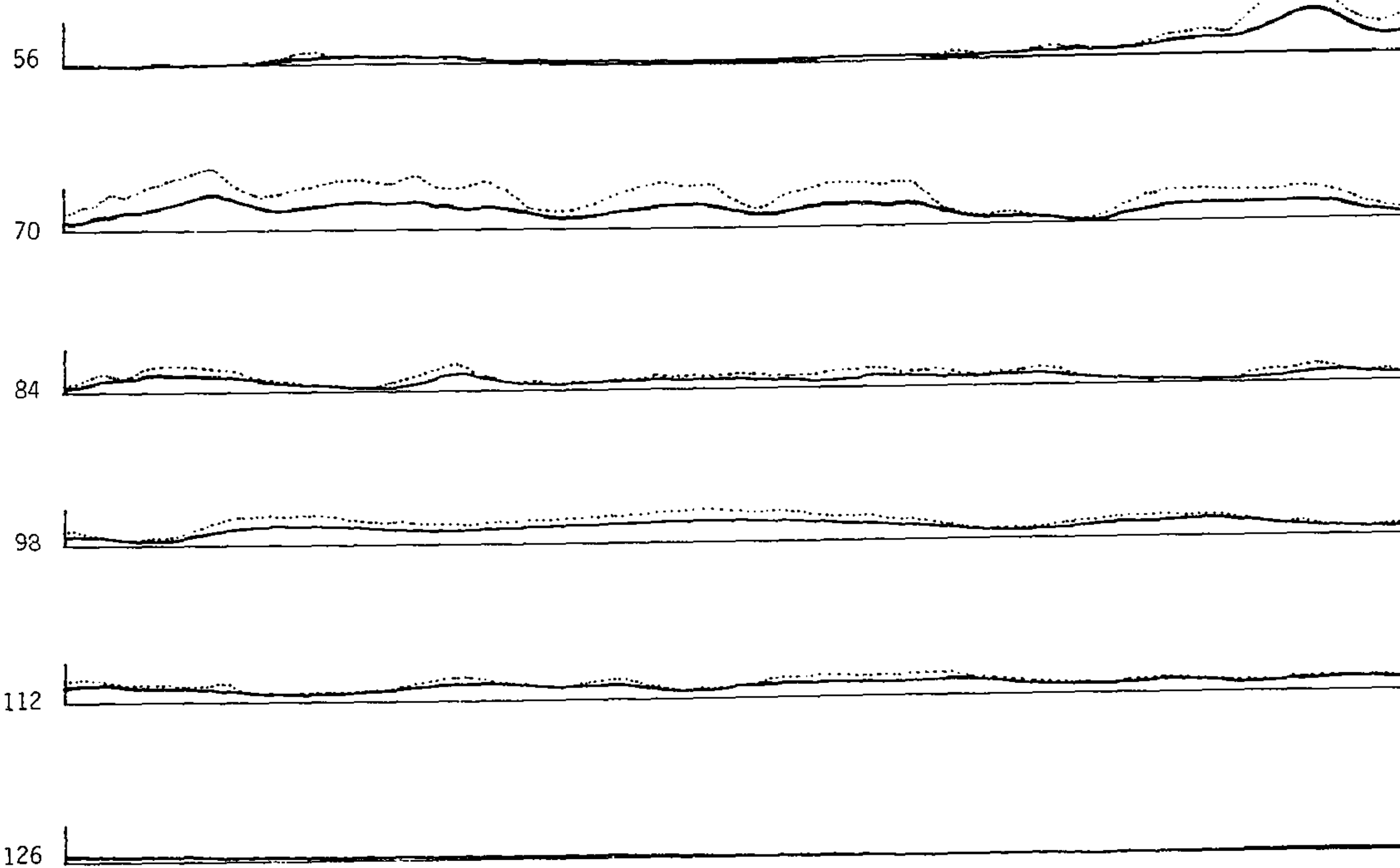
Figure 17 compares the TBDR measurement with the air temperature measurem over the duration of LNG-21. Careful inspection of the peaks and valleys of the top two curves shows qualitative agreement -- that is, the air temperature may provide information on the methane concentration under some conditions.

Figure 18 shows a similar comparison between Laser Sensor #2 data and the air temperature over the duration of the test. Again, a qualitative corr pondence is observed. (It should be emphasized that these data were obta directly from strip-chart records; an analysis of the computer tapes woul provide a comparison limited only by the basic system sensitivity.) The ordinate of the laser sensor measurement is directly proportional to the methane concentration because a logarithmic converter was used on-line to convert the data. It operated in parallel with the infrared detector out which was recorded simultaneously.

A quantitative comparison between methane concentration and air temperatu over a limited time span is shown in Fig. 19, which also contains the dat recorded by Laser Sensor #1. The shape of the temperature curve is seen follow fairly well the methane curve of Sensor #2, although the laser measurement appears to be somewhat slower in tracking. This sluggishness (0.4 sec response time vs. 0.2 sec for the thermister) is due to the relatively slow logarithmic converter used, and not the laser system itse Much faster log converters are available, if needed.



VAPOR TEMPERATURE (THERMISTER MEASUREMENT)
TEMPERATURE
-10
0
10
20
TBDR MEASUREMENT
PERCENT METHANE
16
8
0
TBDR REFERENCE
ARBITRARY UNITS
16
8
0
0
50
100
150



NOTE: NUMBERS REPRESENT TIME (SEC) AFTER START OF SPILL

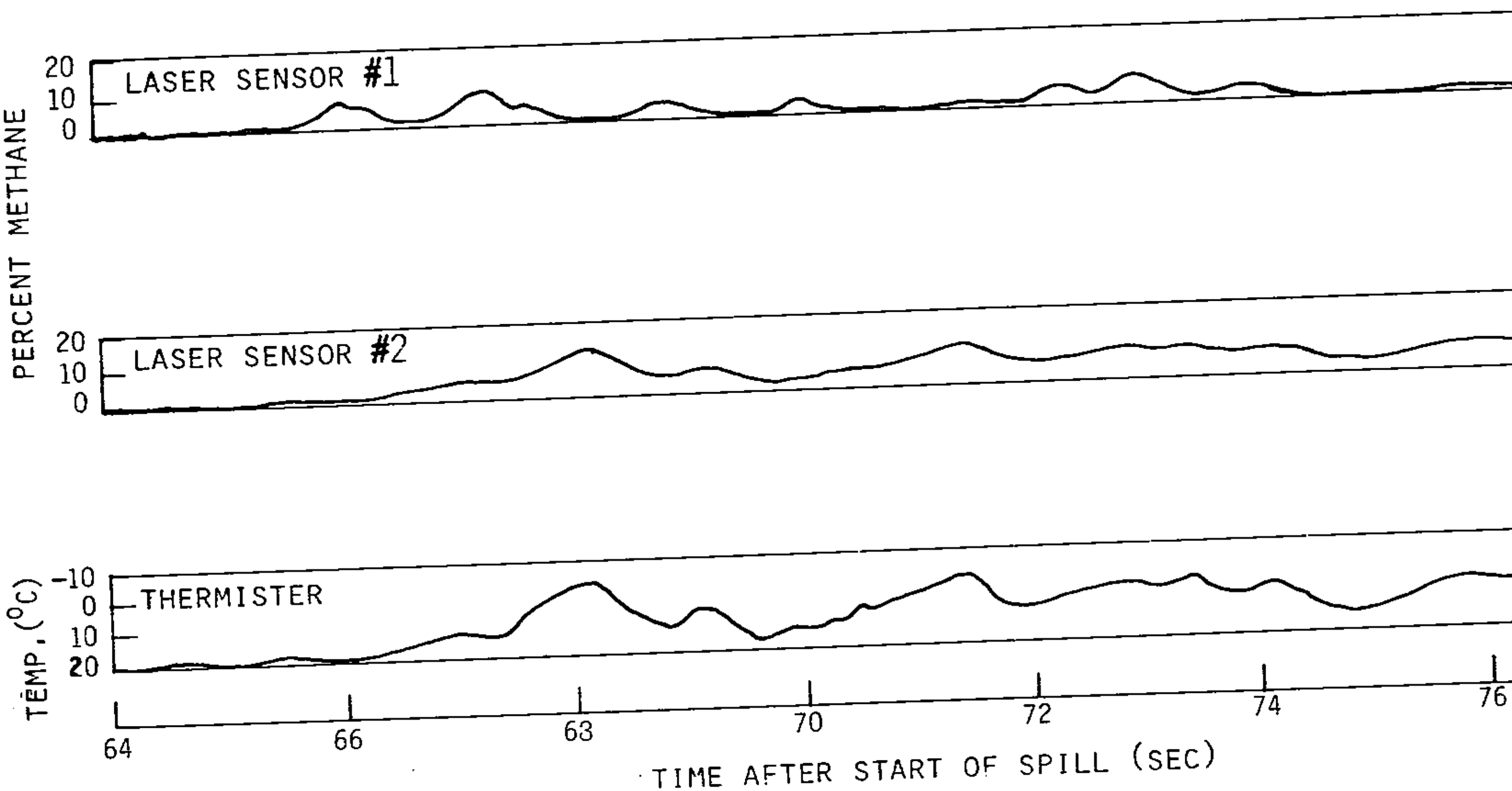
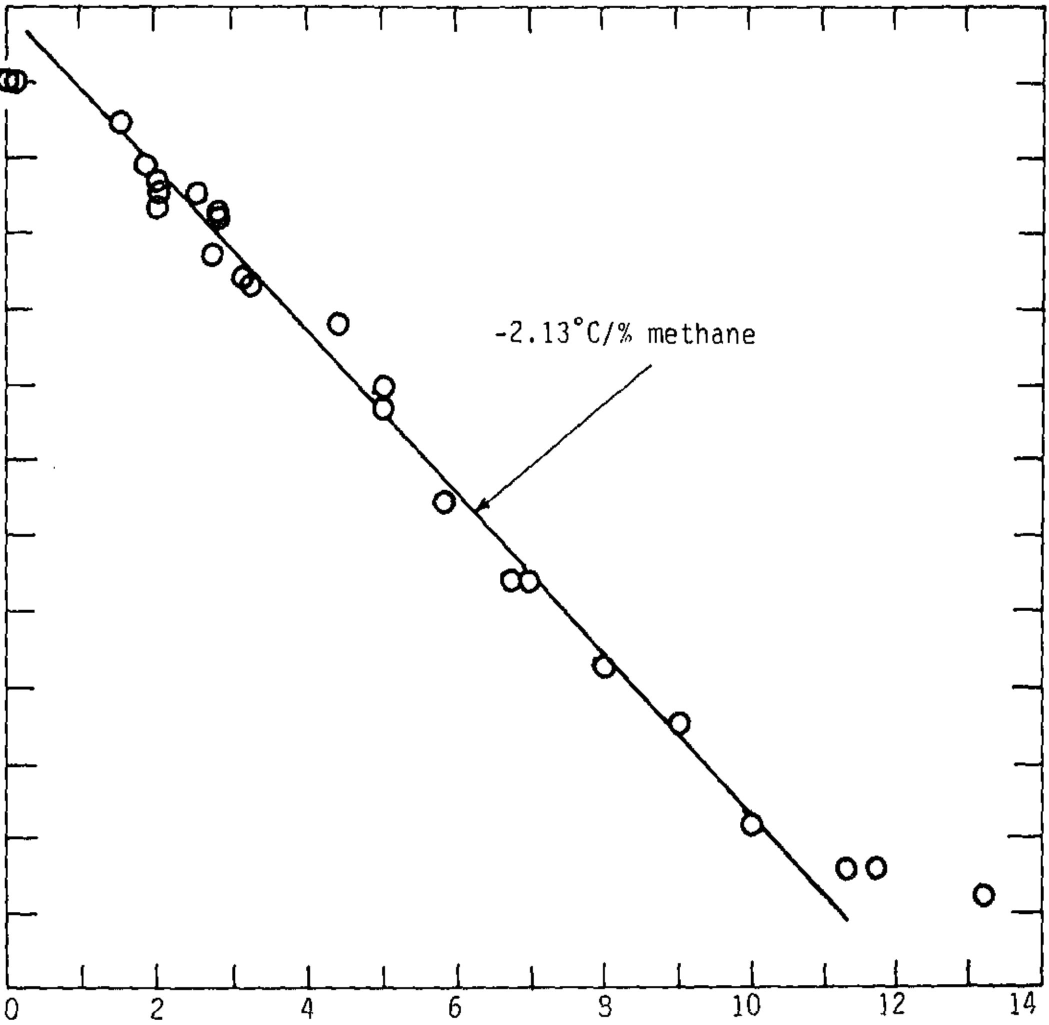


Figure 19. Laser sensor measurements of methane and thermister measurement of air te

data were taken from all regions (times) of the vapor cloud, there do *not appear to be any noticeable systematic effects due to the overall* cooling trend. For larger spills planned in the future, a systematic dependence should be searched for if vapor temperature is to be used as an indicator of methane concentration. From Figure 20 we calculate a dependence of -2.13°C/% methane. This compares very favorably with the theoretical value of -2.22°C/% methane derived by Lloyd Multhauf o LLL. A further discussion of temperature variations of the LNG vapor cloud is given in Report K.

2.3.5 Discussion of LNG-21

Spill Test LNG-21 provided an important comparison between the species specific TBDR and laser instruments, and the non-specific thermister a an indicator of methane concentration. It appears that, under certain conditions and within certain methane concentration ranges, an inexpen sive temperature-measuring instrument can be employed. Good qualitati agreement was also seen between the laser and TBDR measurements; and t experimentally-determined value of the dependence of vapor temperature on methane concentration agreed with the theoretical value.



re 20. Plot of vapor temperature vs. percent methane for LNG-21

3.1 Oxygen Monitoring Instrument

The flammability limits of natural gas (methane as the principal nent) lie in the range of 5 to 15 per cent by volume in air. It lative concentration of the hydrocarbon and oxygen which detc.mi flammability of a mixture of air and natural gas . Consequentl dent measurements of methane and oxygen in the mixture at the si spillage of liquified natural gas (LNG) are important for severa Methods for determining methane concentration have already been the technique of laser absorption as well as by differential IR measurements. It is the purpose of this section to suggest a me oxygen determination.

The method discussed below is based on UV absorption of O_2 in th Runge (B $^3\Sigma_u^-$ - x $^3\Sigma_g^-$) system. Figure 21 shows the absorption co of oxygen as a function of wavelength. It can be seen that oxy appreciable absorption even in the 1900-2000 Å UV range. The ma nents of natural gas are methane and ethane. Table III lists se typical gas analyses for natural gas . Their absorption spect shown in Figures 22a and 22b. They essentially do not absorb U in the above range. Based on these facts, the following experi done to study the feasibility of using the UV absorption techni pendently determine the concentration of oxygen in a mixture of

The experimental set up is shown schematically in Figure 23. A lamp (Oriel Model 6312) is used as the source for UV radiation. from the lamp after collimation by a quartz condensing lens ass (Oriel Model 6304) passes through a 1m long pyrex absorption ce cell is provided with two quartz windows for the incident and t light, and also possesses inlet and outlet ports for the introd different gases. The transmitted radiation is focussed with a focal length quartz lens (f/no. = 4) on the entrance slit of a meter (Oriel Model 7241). The monochromator has a 2400 ℓ/mm ho

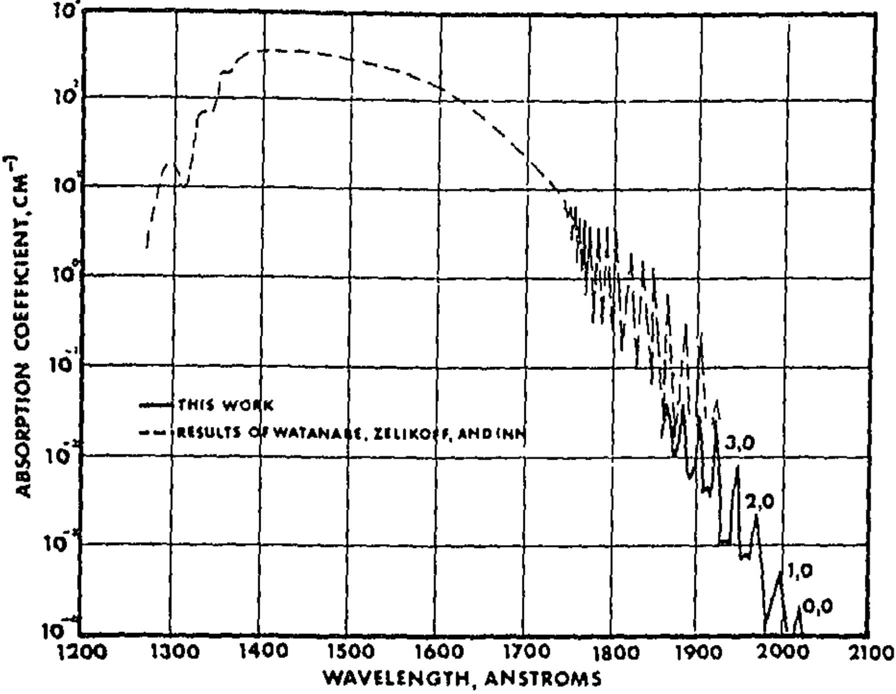


Fig.21 Absorption coefficient of O_2 as a function of wavelength. (from B. A. Thompson et. al., J. Geophy, Res., 68, 6431 (1963))

TABLE III

Composition of Some Natural Gases

Per Cent of Various Components

Sample No.	CH_4	C_2H_6	N_2	CO_2	O_2	Heating Value Btu Per Cubic Foot* at 60 F and 30 in. Hg
1	88.92	3.20	7.68	0.16	0.14	959
2	81.91	17.51	0.11	0.31	0.16	1145
3	98.95	0.00	0.94	0.31	0.16	1000
4	82.86	16.51	0.16	0.31	0.16	1136
5	94.73	2.64	1.89	0.30	0.44	1008
6	66.31	31.70	1.21	0.47	0.31	1240
7	89.04	5.63	4.68	0.21	0.44	1004
8	90.52	4.56	4.29	0.21	0.42	1001
9	98.40	1.00	0.50	0.00	0.10	1016
10	82.60	7.20	7.10	2.70	0.40	967
11	74.20	18.50	7.30	—	—	1085
12	67.90	26.10	6.00	—	—	1157

* Calculated.

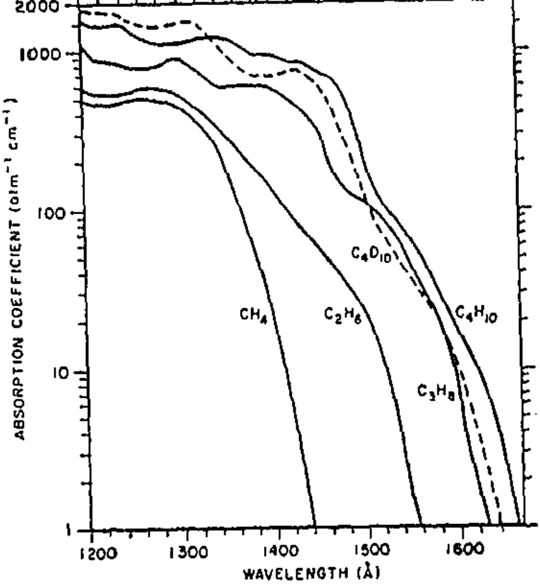


Fig.22a Absorption spectra of some paraffic hydrocarbo
(from H. Okabe, and D. A. Becker, J. Chem. Phys., 39, 2
(1963)

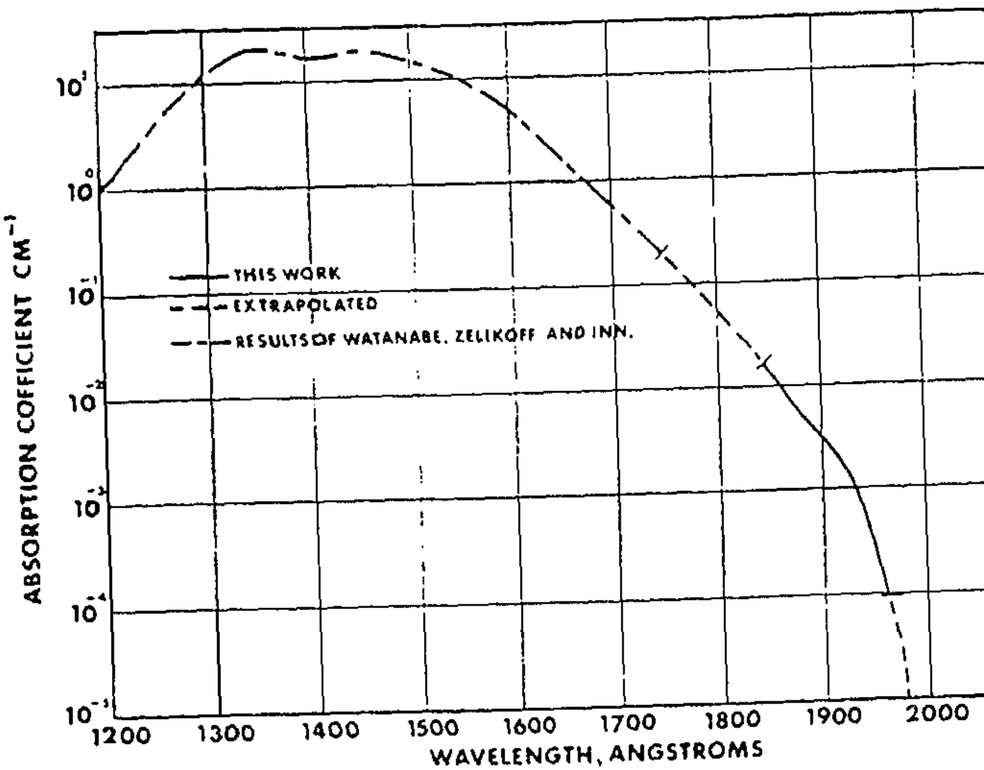


Fig.22b Absorption coefficient of Co_2 as a function of wave
(from Thompson et al., J. Geophy, Res., 68, 6431 [1

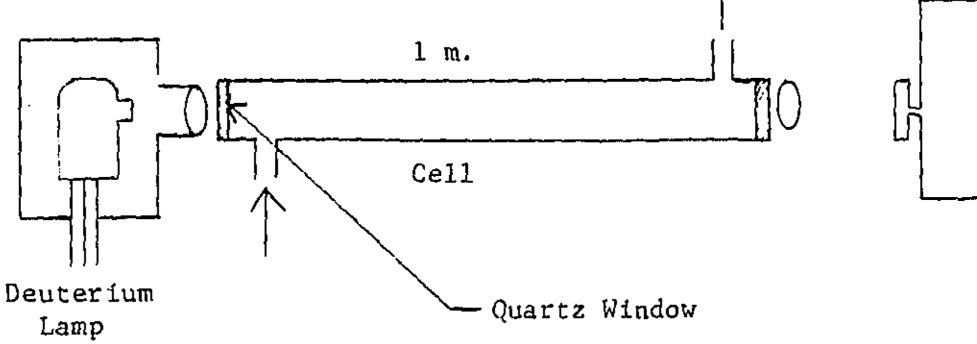


Fig. 23. Experimental Set up for Oxygen Mea

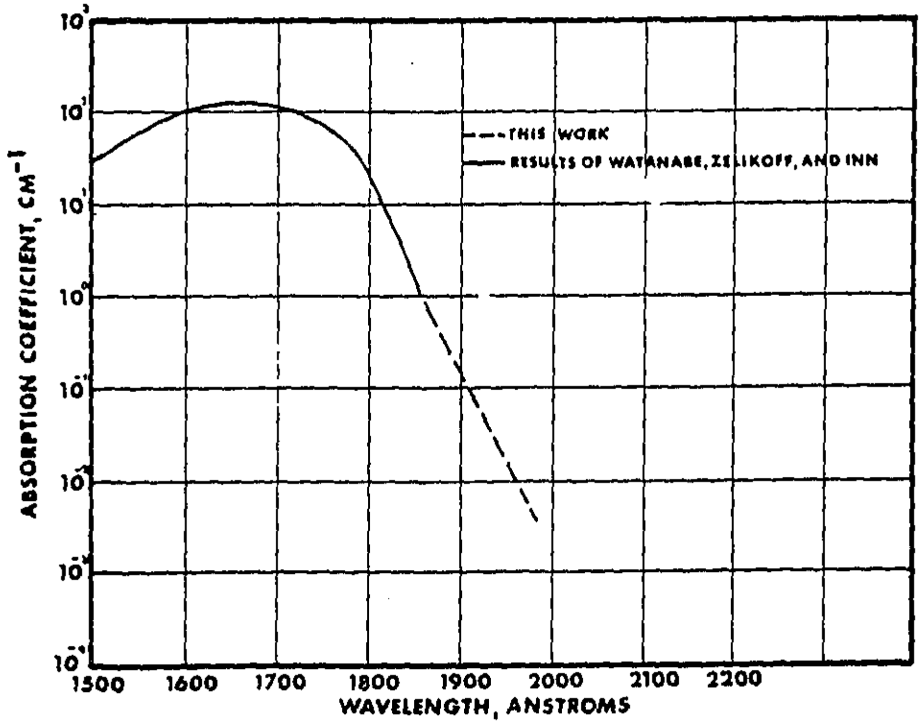


Fig.24. Absorption coefficient of H_2O as a function of waveleng
(from Thompson et al., J. Geophy, Res., 68, 6431 [1963]

ummarizes the results.

1m long column of air at atmospheric pressure has an absorption of abou 0% at 1923 Å. The absorption decreases with the increasing wavelength, nd is about 12% at 1947 Å. Measurement of absorption at any one of these avelengths can be used. However, consideration of interference from oth ases suggests that 1947 Å may be the best choice. In particular, the ab orption coefficient of CO_2 near 1947 Å is of the order of 10^{-4}; it, herefore, has negligible absorption. The absorption of CO_2 is not much ifferent at 1923 Å. Thus CO_2 will not yield any major interference betw 923-1950 Å. The main interferant in the O_2 determination is water vapor hich has significant absorption in this wavelength region (Figure 24). itrogen saturated with water vapor at 1 atm pressure and at room tempera partial pressure of water vapor of about 20 torr) in the absorption cell esults in 4-5% attenuation in the incident light at 1947 Å. It is true hat the interference due to water vapor should be much less than this at hina Lake in view of the fact that it has a relatively dry, desert at- osphere. Assuming a relative humidity of 25%, the error introduced in t easurement will be about 10%. However, this can be accounted for by mak separate measurement of water content. The IR absorption bands of H_2O re well known, and it is possible to determine water vapor by introducin n additional channel at 1.4 or 2.7 μm in TBDR measurements. The change he amount of water from the background due to the influx of LNG vapor, w ubtracted from O_2, will yield the concentration of oxygen.

hus, an independent O_2 measurement can be made by UV (1923-1947 Å) ab- orption. The interference of water can be eliminated by using a separat R measurement.

.2 Infrared Fiber Optics Research

rogress has been made since the preliminary results of the month of June 978. During that time we computed the "numerical apertures" of the liqu

Table IV. Absorption measurements at several UV wavelengths for dry ai
oxygen, and nitrogen saturated with water vapor at room temp
ture.

	Percent Absorption		
λ (Å)	DRY AIR	OXYGEN	WATER-SATURATED N_2
1923	20	60	11
1947	12	40	4
1971	4	--	1

Since then we have modified the optical system design as follows:

i) We have used a Spectra Physics He-Ne laser, Model 124/B operating at 3.39 μm wavelength with a power output of 6 mWatts (measured). This increased the signal at the output of the fiber to an easily-detectable level.

ii) We used an Indium Arsenide detector (Judson Infrared), which operates with much improved sensitivity, compared to pyroelectrics. This is one of the few infrared detectors which has peak responsivity at around 3.4 μm, the wavelength at which we are operating.

iii) A smaller size hypodermic needle (#26g) was used. This enabled the quartz fiber to be straighter while inside the window system.

iv) We have incorporated a micropositioner in the system to hold the window-fiber assembly for both the input and the output ends of the fibers. In this way we can precisely adjust the penetration of the laser light into the fiber waveguide as well as fine-position the output end of fiber to get maximum signal.

With the modifications in the experimental set up described above, the transmission loss in the liquid-core hollow fibers was measured. The liquid was tetrachloroethylene ($C_2C\ell_4$). The output of the fiber end wa measured by the InAs detector. The detected output signal was measured a function of the fiber length by cutting successive pieces from the or 16-meter length. The results are shown in Figure 25. The data points with NG-1 and NG-3 filters were taken to measure the losses with attenu laser light. From the slope of the curve, we calculated the transmissi of this liquid-core fiber to be 56.2 db/km.

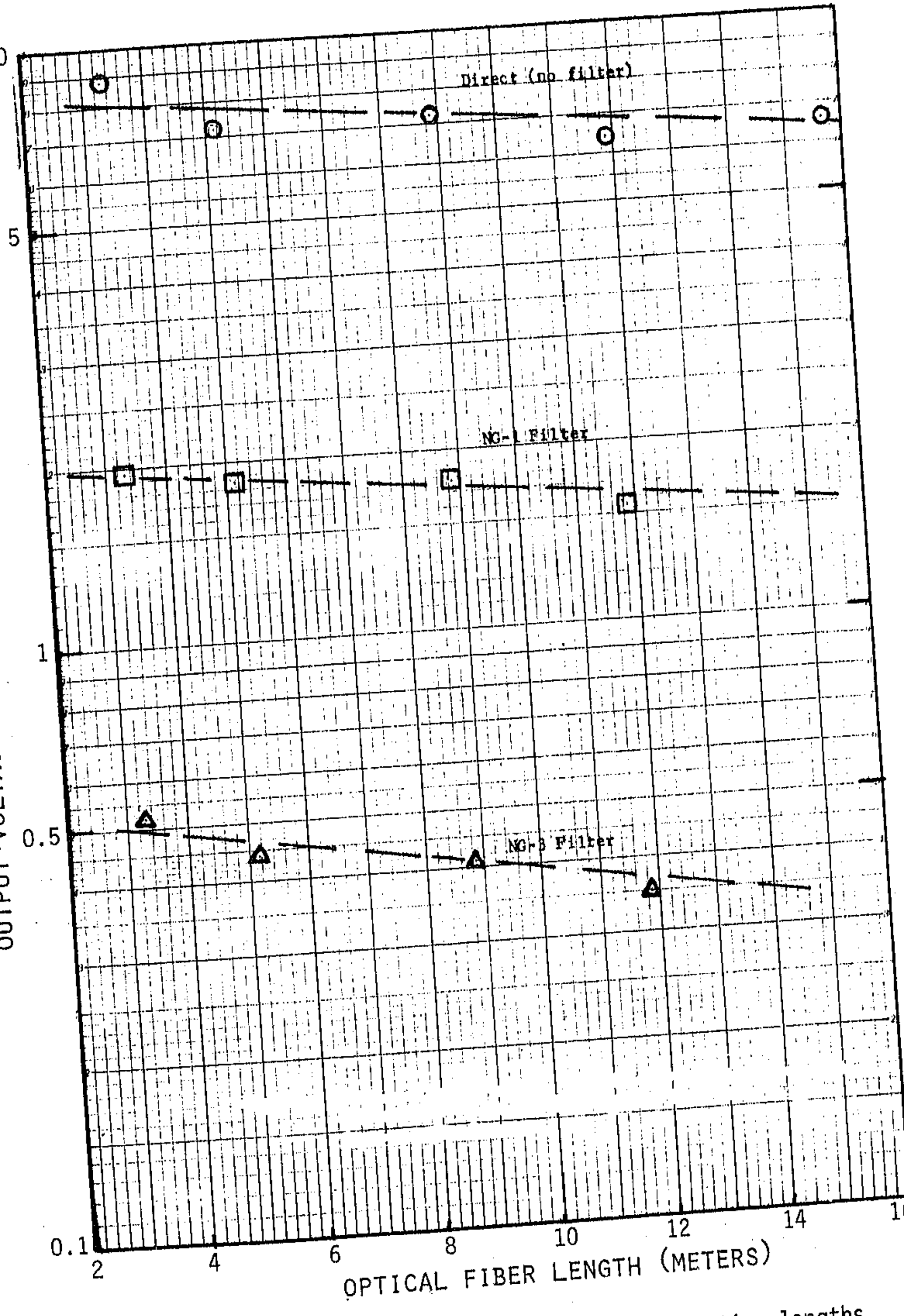


Figure 25. InAs detector signal for various fiber optics lengths

Two types of instruments for the detection of methane in LNG spill vapo were developed, tested, and operated in the field. The two-band differ radiometer (TBDR), based upon a nondispersive infrared technique and us a 20-cm path within the vapor cloud, detected methane concentrations as at 1% with a time constant of 0.15 seconds achievable. The laser instr ment provided measurements of methane at two locations separated vertic by one meter, and used a 2-cm path in the vapor cloud. Its system sens vity is 0.1% methane, and speed is 0.005 seconds (0.01 seconds if used a strip-chart recorder). Both instruments provided real-time data of S Tests LNG-18, 19, and 21. The laser instrument incorporated a thermist for rapid measurements of air temperature. The data obtained and descr in this Report are duration, extent, and intensity of the methane-laden vapor clouds and their temperature as a function of time. Some of the results are tabulated in Table V on the following page, which includes analysis of the fraction of time the methane concentration exceeded 5%. Laboratory research on the development of another instrument for the detection of oxygen showed that the TBDR principle can be employed. Progress was also made in the development of infrared fiber optics, whi may permit the utilization of more cost-effective techniques for the me ment of methane and other vapor constituents.

Table V. Summary of Results of Spill Tests

	LNG-18		LNG-19		LNG-21	
	1.5 m	2.5 m	1.5 m	2.5 m	1.5 m	2.5
First Vapor Cloud						
Time from spill (sec):	40.2	40.2	40.4	40.4	57.2	57
Duration (sec):	4.6	2.4	1.5	1.0	1.5	[illegible]
Peak CH_4 conc. (%):	10.9	11.1	1.28	0.28	3.8	[illegible]
Time above 5% CH_4 (%):	30.	26.	0	0	0	[illegible]
Second Vapor Cloud						
Time from spill (sec):	61.4	61.4	93.2	95.0	64.2	6
Duration (sec):	41.0	39.4	3.8	1.0	63.2	6
Peak CH_4 conc. (%):	14.2	11.4	1.46	0.44	13.5	[illegible]
Time above 5% CH_4 (%):	35.	6.3	0	0	27.	
Third Vapor Cloud						
Time from spill (sec):			105.2	105.2		
Duration (sec):			0.12	0.28		
Peak CH_4 conc. (%):			0.12	0.14		
Time above 5% CH_4 (%):			0	0		

Note: The 1.5 m and 2.5 m column headings refer to the height of th
above the ground.

D. Norris, J. Peterson, G. Reisdorf, D. R. Rupnik, C. Rutledge, M. S. S
N. K. Simon, M. P. Sinha, J. Riccio, and R. A. Zanteson.

We are indebted to Doug Lind of the China Lake Naval Weapons Center fo
assistance in performing these spill tests. We also express appreciat
to the Lawrence Livermore Laboratory personnel for use of their traile
for the JPL data recording system and for general support. In particu
we thank Ron Koopman for providing LLL data for LNG-18 quoted in this
Report.

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one phase of research carried out at the Jet Propulsion Laboratory, Ca
Institute of Technology, under contract NAS 7-100, sponsored by the Na
Aeronautics and Space Administration.

REPORT R

A Review of the 1978 China Lake LNG Dispersion Experiments and Instrumentation

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L. G. Multhauf
G. E. Bingham
D. N. Frank

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract W-7405-Eng-48

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Livermore, California 94550

REPORT K

TABLE OF CONTENTS

FIGURES

TABLE

LNG clouds in the four spill experiments at China Lake this summer and f
We wished to evaluate the instruments under adverse field conditions, an
take some useful data on the dispersion of LNG vapor.

A grab sampler system was designed and built by LLL for use as a reference for the other instruments. It worked well and gave us confide in the other measurements which would have been hard to justify without absolute reference. The Shell and TSI sensors were based on the princip of hot wire anemometry. Both worked well in general but had certain draw backs. The Shell sensor was flow sensitive while the TSI was not since utilized choked flow through an orifice at sonic velocity. The TSI had much faster time response than the Shell. Both sensors were noisy. Bo sensors must be isolated from the water droplets condensed from the air the cold LNG. This was done by pumping the sample through coiled copper tubing in a warming bath before it reached the sensor, a solution which involved a lot of cumbersome hardware. Similar to these was the MSA sen which used a hot catalyst coated wire and had a very slow response time.

Two sensors based upon the characteristic absorption of infrared radiation by the hydrocarbon species of interest were tried. One of the was a commercial device manufactured by Anarad Incorporated and the othe was an LLL developed miniature prototype. The Anarad device was slow an required that the sample be free of condensed droplets. It did, however detect methane, ethane, and propane. The LLL device was faster and was able to operate directly within the LNG vapor cloud.

A Raman LIDAR was used on one spill test. The results were promis in that it worked well in regions where there was no fog, i.e, where the methane concentration was less than 15%.

luction

Our primary purpose for participating in the LNG dispersion experiment
ina Lake this summer and fall was to evaluate instruments which might
ed to measure methane concentration and other parameters of interest
g future, larger scale spill experiments. This evaluation involves an
-comparison of the instruments under adverse field conditions as well
estimate of their adaptability to future needs. Our criteria include
response, i.e. the ability to follow the turbulent eddies within the
cloud, the ability to detect the principal hydrocarbon species presen
NG, and insensitivity to the LNG produced fog and low temperatures. In
tion we have taken some useful data on the dispersion of LNG vapor
uding the observation of turbulence effects and differential boil off o
different hydrocarbon species. These experimental data will soon be
ared with calculations which will help us determine what will be
rtant for the larger scale experiments.

This report contains some data from all four of the LNG dispersion
s performed at China Lake. We will rely heavily on the first test,
ver, because it has been much more extensively analyzed than the other
e. A short summary of the conditions under which the four experiments
performed is given in Table 1. The wind data indicate the
ability in both direction and speed observed at different places at

Table 1 A Summary of the Environmental Conditions for

The 1978 China Lake Dispersion Tests.

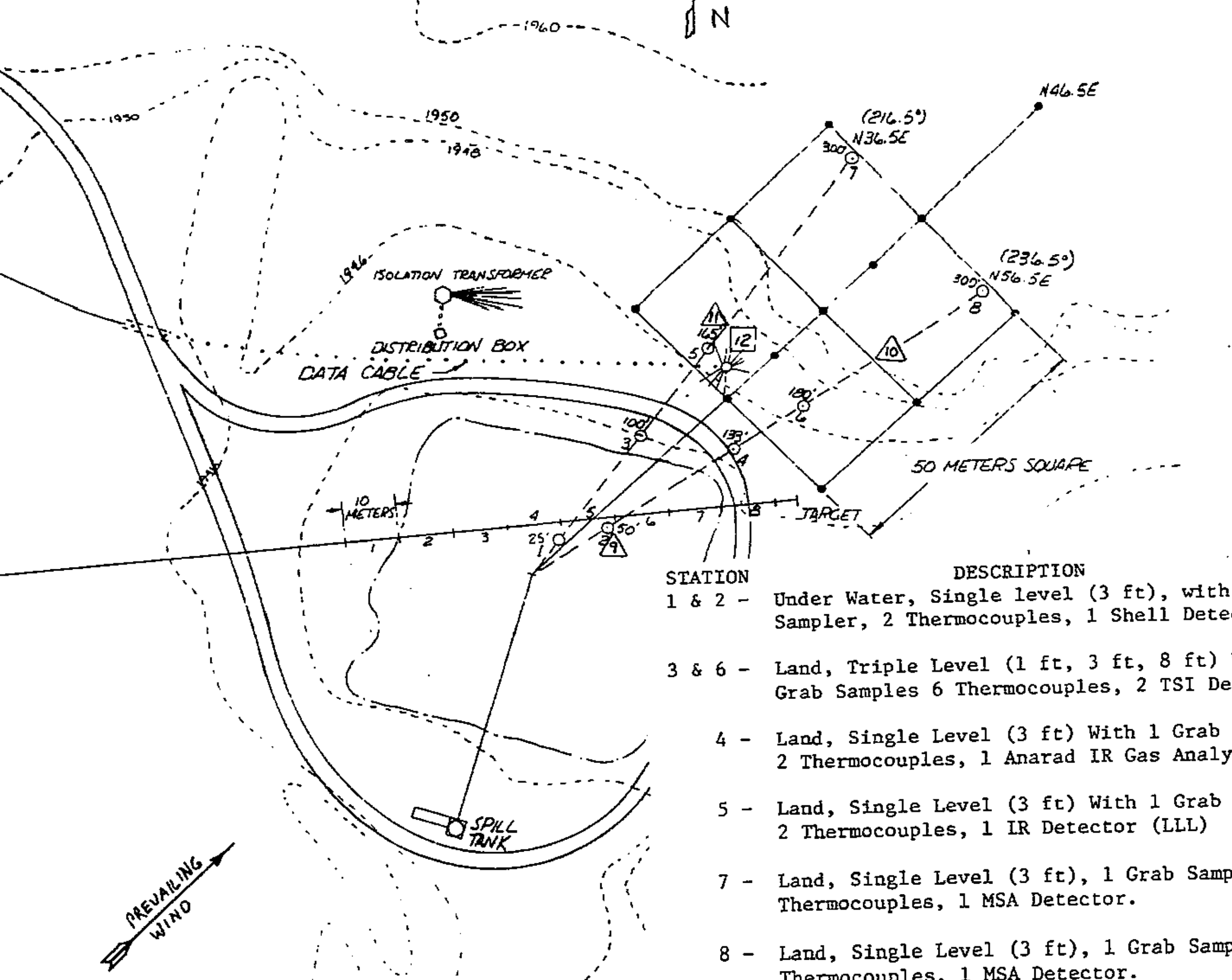
	LNG-18			LNG-19	LNG-20		
	31 August			13 September	9 November		20
	14:56			19:37	15:26		
ature	35.8°C			21.1°C	26.8°C		
umid.	16%			29%	15%		
/olume	$4.39m^3$			$4.52m^3$	$4.5m^3$		
Duration	67 sec.			59 sec.	77 sec.		
Time (sec)	0-50	50-100	100-150	0-150	0-75	75-150	
ion 9	190°	210°	175°	239°	244°		
11	205°	210°	185°	257°	252°		
10	220°	200°	190°	281°	249°		
wer-2m	212°	212°	220°	260°	256°		
er-10m	212°	207°	232°	257°	256°		
9(m/s)	3.8	1.5	3.5	2.2	5.4	6.2	
1	4.5	3.0	4.0	3.7	7.5	9.0	
0	6.3	5.0	6.5	5.01	10.0	11.8	
wer-2m	6.3	5.6	7.6	4.9	8.5 - 15		
er-10m	8.0	6.7	11.2	4.9	---		
ity	Unstable			Stable			
	yes			yes	yes		
	no E			yes	yes		
	trouble			no	yes		
	no			yes	yes		
	no			yes	no		
	yes			yes	yes		
ampler	OK			4, 6 triggered early	OK		
ts				gas missed 5, JPL, 7	gas missed 5, JPL, 7		

the spill site. The detectors which were working for the various spills are listed at the bottom. It took all four experiments to get good operational data on all of the detectors being evaluated.

Our intention upon arriving at China Lake in August was to do at least one experiment per week until the series of five or six experiment was complete. The weather did not cooperate with this plan, however. Specifically, the sustained south-west wind necessary to perform the experiments did not occur during the second half of September, the entir month of October, or the first week of November. As a result of these delays, the data from all four tests have not yet been completely analyz and consequently this instrumentation evaluation is not yet complete. based largely on the data taken on the first two tests. We do not expec changes in general conclusions about the test results but some of the de may change when the analysis is completed.

The Experimental Configuration and Data Recording System

Our array of eight stations was laid out as shown in Figure 1. Thi array was supplemented by instruments fielded by JPL and by an array of detectors and thermocouples fielded by Lind, also shown in Figure 1. A more detailed sketch of our instrument placement at each station is show Figure 2 for LNG18 and 19. Figure 3 is a composite of four photographs of instrument stations. Figure 3a is a view of the water Stations 1 and These stations each contained a shell detector and a grab sampler at abo 3 feet above the water and two thermocouples, one at 2 feet and one at 3 feet. The boxes containing the sensors, grab samplers, and electronics



STATION	DESCRIPTION
1 & 2 -	Under Water, Single level (3 ft), with 1 Grab Sampler, 2 Thermocouples, 1 Shell Detector.
3 & 6 -	Land, Triple Level (1 ft, 3 ft, 8 ft) With 3 Grab Samples 6 Thermocouples, 2 TSI Det.
4 -	Land, Single Level (3 ft) With 1 Grab Sampler, 2 Thermocouples, 1 Anarad IR Gas Analyzer.
5 -	Land, Single Level (3 ft) With 1 Grab Sampler. 2 Thermocouples, 1 IR Detector (LLL)
7 -	Land, Single Level (3 ft), 1 Grab Sampler, 2 Thermocouples, 1 MSA Detector.
8 -	Land, Single Level (3 ft), 1 Grab Sampler, 2 Thermocouples, 1 MSA Detector.

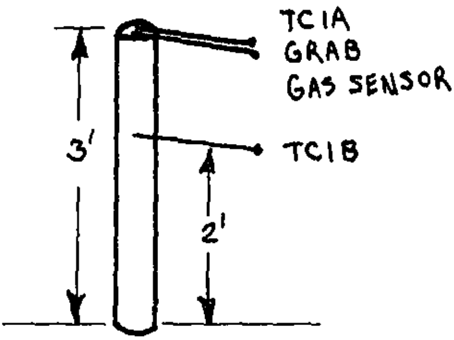
he China Lake LNG spill

FIGURE 2

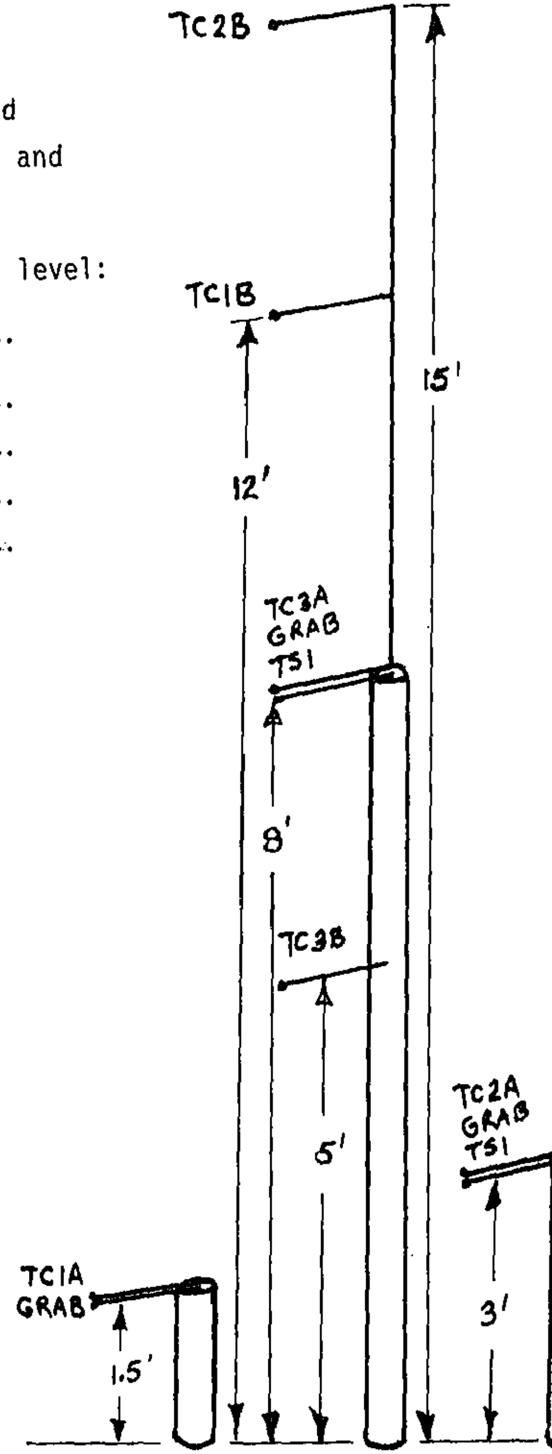
Thermocouple, grab sampler, and gas sensor locations for LNG20 and 21.

Station base height above pond level:

<u>Station</u>	1 & 2	-	0 ft.
"	3	-	2 ft.
"	4	-	5 ft.
"	5 & 6	-	7 ft.
"	7 & 8	-	20 ft.



Stations 1, 2, 4, 5, 7, 8



Stations 3 & 6

GURE 3a Stations 1 and 2

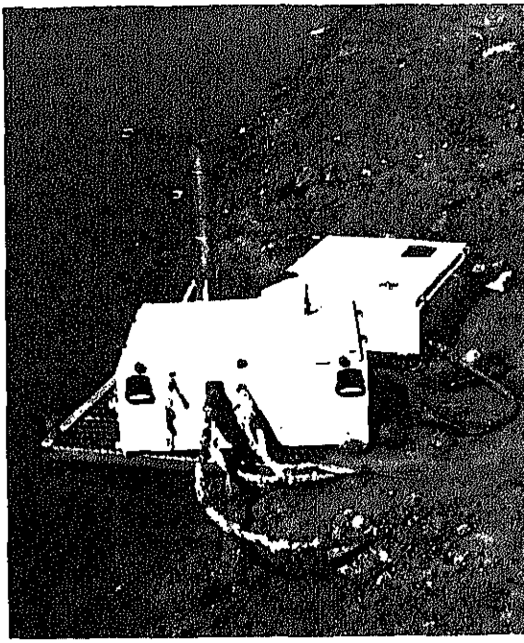
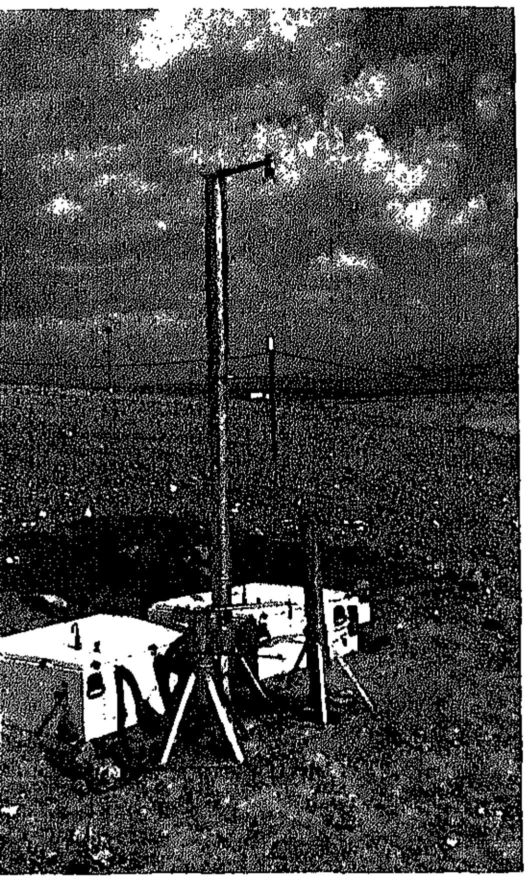


FIGURE 3b Station 4



are under water. Figure 3b shows the triple level Station 6. This station contains two TSI sensors, at the 3 and 8 foot levels, 6 thermocouples at varying levels and 3 grab samplers at the 1.5, 3 and 8 foot levels. The tall pipes contained water which was used to warm the cold gas as it flowed through coiled copper tubing within the water bath. The gas sensors and the grab bottles were located inside the air-tight, NEM4, white boxes, next to the sampling towers. These boxes were purged with nitrogen during the tests to make sure that no methane could find i way to an ignition source. Figure 3c is a picture of Station 4 at the edge of the pond, where it was for the first two tests. It was moved further up the hill for the two later tests. This station contained the Anarad IR detector and a grab sampler at about 3 feet above water, and two thermocouples, at 2 feet and 3 feet above the water. A picture of one of the furthest out stations, Station 7, is shown in Figure 3d. These stations contained an MSA detector, a grab sampler, and two thermocouples.

Figure 4 is another composite picture showing some of the relevant details of the instrumentation stations. Figure 4a shows the inside of Station 1. The metal cylinder in the center is the shell detector head its electronics package in the upper left. The grab sampler system is c the right, with the programmable controller across the bottom of the box Figure 4b is a close-up of the intake ports, with the thermocouple in its solar shield and the intake for the gas sensor and the grab sampler. Figure 4c shows the inside of the Anarad IR detector, showing the three optical benches in the upper right of the box. Figure 4d shows the

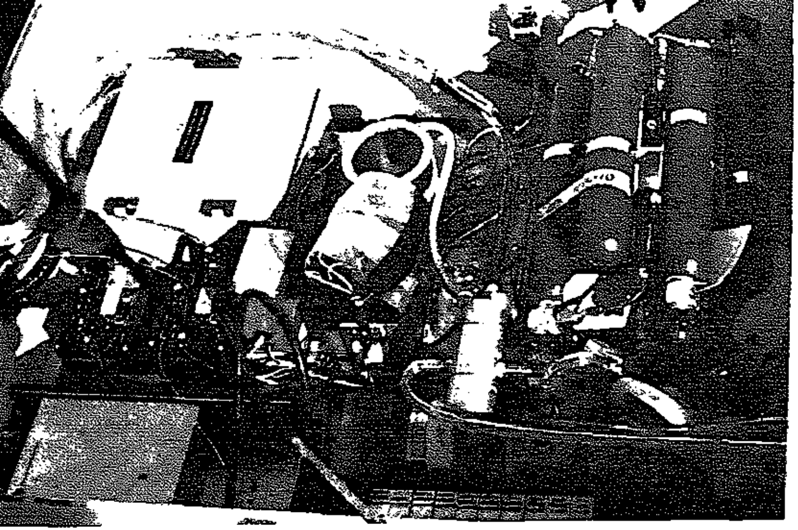


FIGURE 4a Station 1 with Shell detector

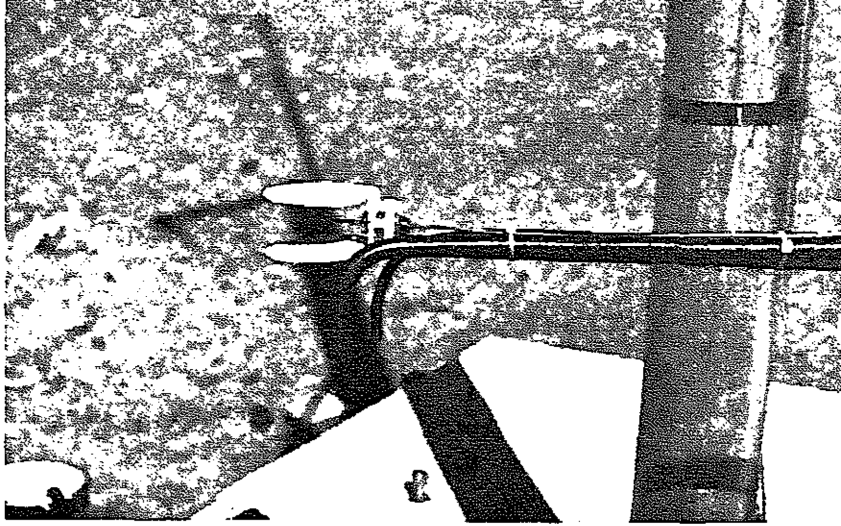
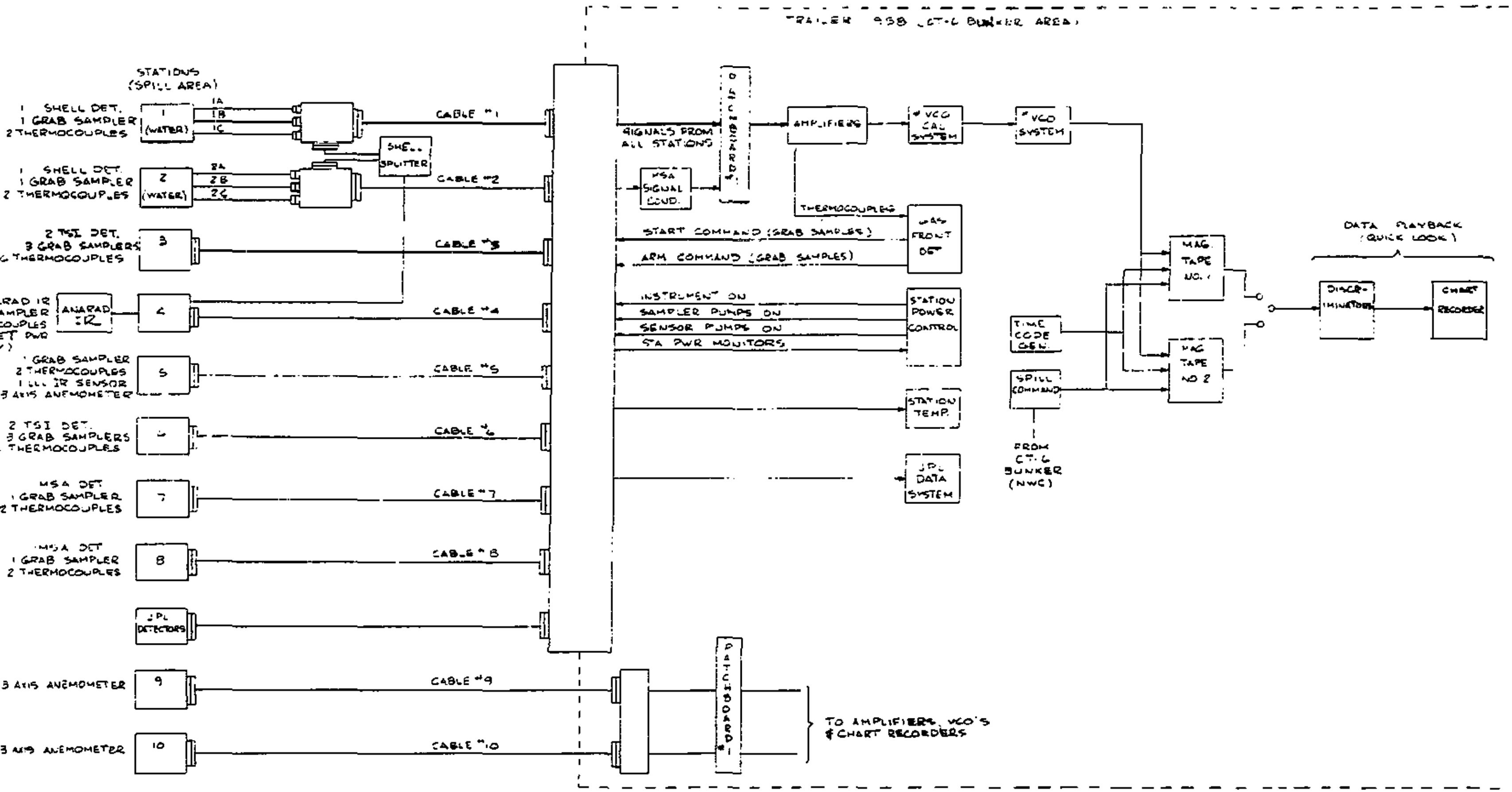


FIGURE 4b Intake port with thermocouple

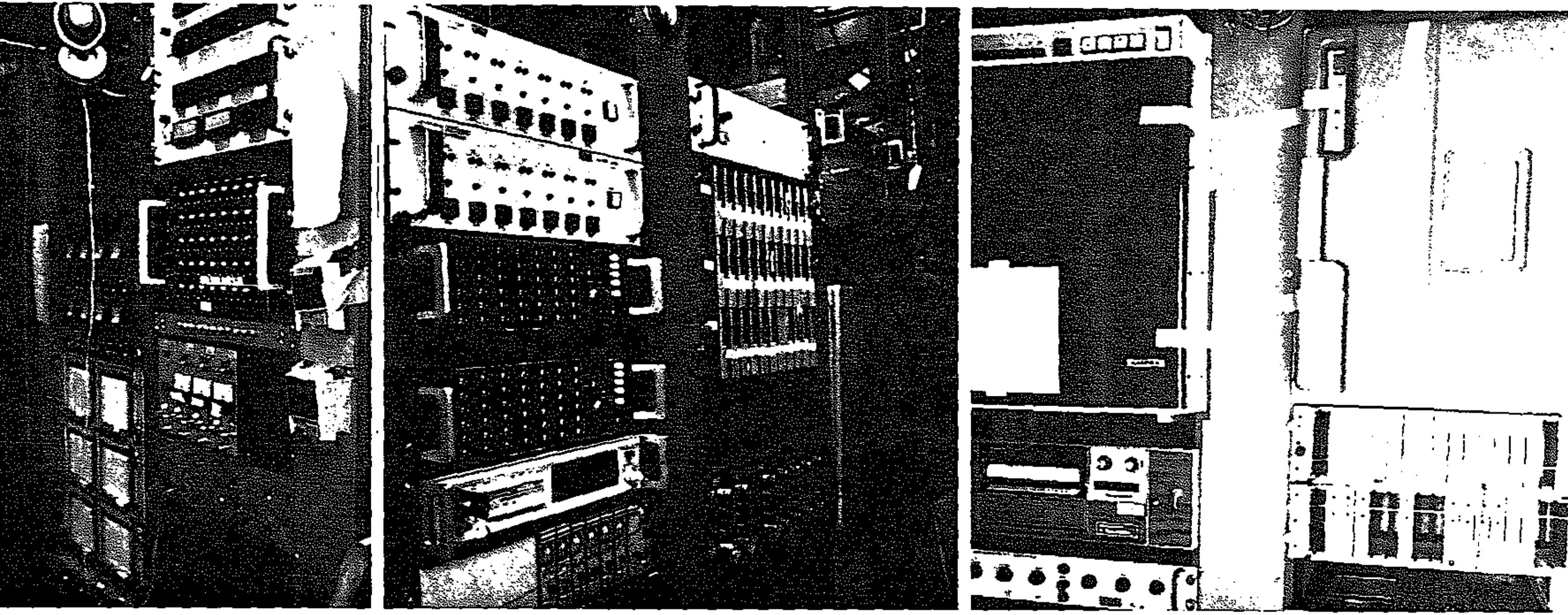
nside of Station 3, a triple level station. The three grab sampler syst nd pumps are in the box on the left. The TSI detectors, their electroni nd the programmable controller are in the box on the right.

A block diagram of the data aquisition system used for the China La spill experiments is shown in Figure 5. All of the data, command, and onitor signals were transmitted to and from each of the eight stations c ulticonductor cables. Remote control of various station functions and t ata recording system was located in the electronics trailer, approximate 00 feet from the spill point. A series of photographs of the rack mount nstruments are shown in Figure 6. Figure 6a shows the various control nd monitor panels. In the rack furthest to the left, on the top, is the onitor screen, below are the temperature controllers, connected to therm ouples at the inlet port of each station, and used to trigger the grab amplers when cold gas arrived at the station. Below that are the chart ecorders used to monitor the wind velocity and direction before, during, fter the spill.

In the next rack to the right and at the top in Figure 6a are the emperature displays used to monitor station temperature because of conce hat some of the temperature sensitive electronic components would be amaged or not function properly if the box temperatures got too high. B his is the main control panel for turning on all of the various instrume nd associated pumps in the eight stations. Below this are the meter rea uts for the MSA detectors at Stations 7 and 8. These were useful for etermining when gas arrived at these stations so that the grab sampler



* VCO - VOLATAGE CONTROLLED OSCILLATOR



(a) (b) (c)

IGURE 6 The inside of the electronics trailer showing the station monitor and control equipment in (a), the amplifiers, VCO's, and calibrators in (b), and the tape recorders in (c).

always low enough for the temperature controllers to trigger the sampler system. The next picture, Figure 6b, shows the JPL instrumentation at th far left. A description of this instrumentation is contained in Report J

Each data signal was connected to an amplifier in the trailer. The are located in the second rack from the right in Figure 6b. The frequenc response of the amplifiers was limited to about 10 Hz for all of the inst ments except the TSI detectors. The ouputs from the amplifiers were conn in group of six, to voltage controlled oscillators (VCO's). These are lo in the two upper most units in the rack furthest to the right in Figure 6 Each group of six VCO's were then multiplexed together to form a single composite signal which was recorded on one of 12 tracks of a magnetic tap recorder. This recorder and its backup are shown in Figure 6c. The data system capacity was, therefore, 6 x 12 = 72 channels. The tape recorders used were 14 track machines, so that the spill command signal, by itself recorded on track 14 and a time code signal was recorded on track 13. Th modules in the middle of the right most rack in Figure 6b are custom buil calibrators for the system. These were used to put voltage calibration steps on tape immediately prior to the spill experiments.

Extraction of the data from the tape was accomplished by playing th tape back, one track at a time, into six discriminators corresponding to each of the six VCO frequencies recorded. These discriminators are shown in the lowest module of the far right rack in Figure 6b. All of the data

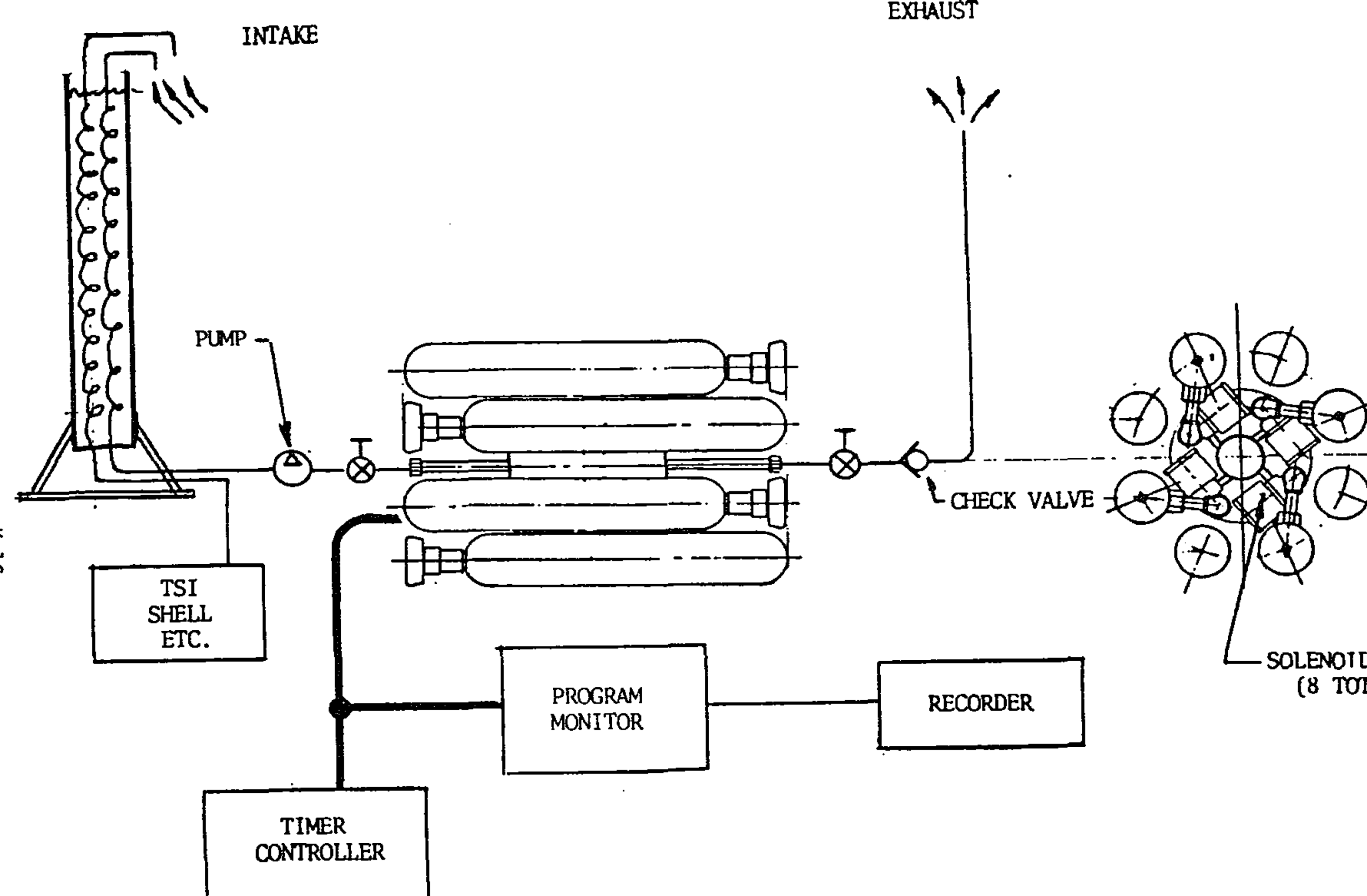
ere played back on an oscillograph in the trailer (beneath the main tape ecorder in Figure 6c) for a quick look immediately after the experiment. ome of the more interesting or important data channels were then played ack on a chart recorder in the trailer for more detailed analysis. The ain data reduction effort, however, was performed back at LLL, first in -Division Analog Data Center where the analog signals were unscrambled a igitized and then on the OCTOPUS digital computer system. These data fi re now stored in the mass storage device which is part of this system ar re available to all personnel in the LNG Program.

ne Gas Detection Instruments

In this section we will discuss the various instruments which we us uring the LNG vapor dispersion experiments. For the purpose of discuss nstrument performance, we will also present some of the data taken by ea nstrument during these tests, but will not attempt to present all of the ata taken, or to give much analysis of the data.

rab Sampler

This is an LLL designed system using a TI (Texas Instruments) progr ble timer to open solenoid valves on a series of evacuated lecture bott chematic diagram of this system is shown in Figure 7. Cold gas enters a he intake port, flows through smooth coiled copper tubing in a water bat he intake tower, such that it is warmed to ambient temperature, and then hrough the sampler manifold. The flow path is designed such that it cor o rough surfaces, sharp bends, discontinuities, or plenums which would


INTAKE
EXHAUST
PUMP
CHECK VALVE
SOLENOID
(8 TOT
TSI
SHELL
ETC.
PROGRAM
MONITOR
RECORDER
TIMER
CONTROLLER

luce mixing and result in a loss of time correlation with the gas conce

on measured. The bottles are arranged radially around this manifold. Th

imer opens the solenoid valves at pre-programmed intervals of time. Th

into the bottles is limited by an orifice such that the flow rate is

rant over the time interval that the bottle is open. Orifices are

d so that the final pressure in the lecture bottles is about 0.25

spheres. The bottle then contains a gas sample representative of the

age gas concentration flowing past the intake port during the sampling

e. The system was designed for intervals between 0.6 and 10 seconds.

sequence was initiated automatically from the spill valve command for

tions 1 and 2 and either manually or by a thermocouple controller, trig

ed by the arrival of the cold gas, at the other stations. The grab sam

ling intervals were set to either take short samples for point compar-

on with the faster responding sensors or longer samples for time averag

mparison. Station 7, for instance, was programmed, for some of the test

ke a series of eight, 10 second samples, one immediately after the othe

vering essentially the entire time that the gas cloud was present.

Analysis of the gas in the bottles was performed at LLL on a mass

pectrometer. The system has been designed to give at least a 93% pure

he stagnant gas volume in the orifice and tubing is only 3% of the gas

olume taken with the bottle. The errors associated with the mass spec

neter analysis are generally much less than this. Uncertainties of the

of 1% of the measured value might be considered typical.

A grab sampler was installed at every gas sensor location with th

intention of comparing gas sensor measurements with grab sample measur

r each test. The tubing and pump characteristics were such that the time required for the gas to flow from the intake port to both the gas sensor and the grab sampler was approximately 1.7 seconds. This allows direct comparison between grab sampler and sensor data.

hell Detector

This instrument was developed by Shell Research Ltd. and is essenti forced flow version of the MSA detector. We are most grateful to Shell esearch Ltd. for loaning us this sensor for use on these experiments. T ensor operates on the principle of heat loss from a heated filament expo o the gas/air mixture. This element and another, exposed only to air at mbient temperature, make up two arms of an electrical bridge circuit. A hange in gas concentration will result in a change in the rate of heat ransfer from the filament exposed to the gas stream if the heat capacity pecific heat of the gas differs from that of air. The isolated filament elps compensate for temperature changes of the housing. The changing emperature of the exposed filament results in a changing resistance and ignal from the bridge. This is routed through a signal conditioning cir nd recorded in the electronics trailer. The shell detector at Station 2 s shown in Figure 4a.

The response time of this sensor appears to be about 0.7 seconds, a easured during laboratory calibration. The instrument was calibrated fo o 100% methane in the laboratory and re-calibrated periodically during t xperimental series. The output was somewhat nonlinear with gas concentr ion over the full 0-100% range and extremely sensitive to flow rate thro

housing. This problem was mitigated somewhat by installing an orifice
he line but frequent calibration checks were still considered necessary.
e on the signal was found to be about + 2% of full scale and was
ributed mostly to gas turbulence inside the sensor housing.

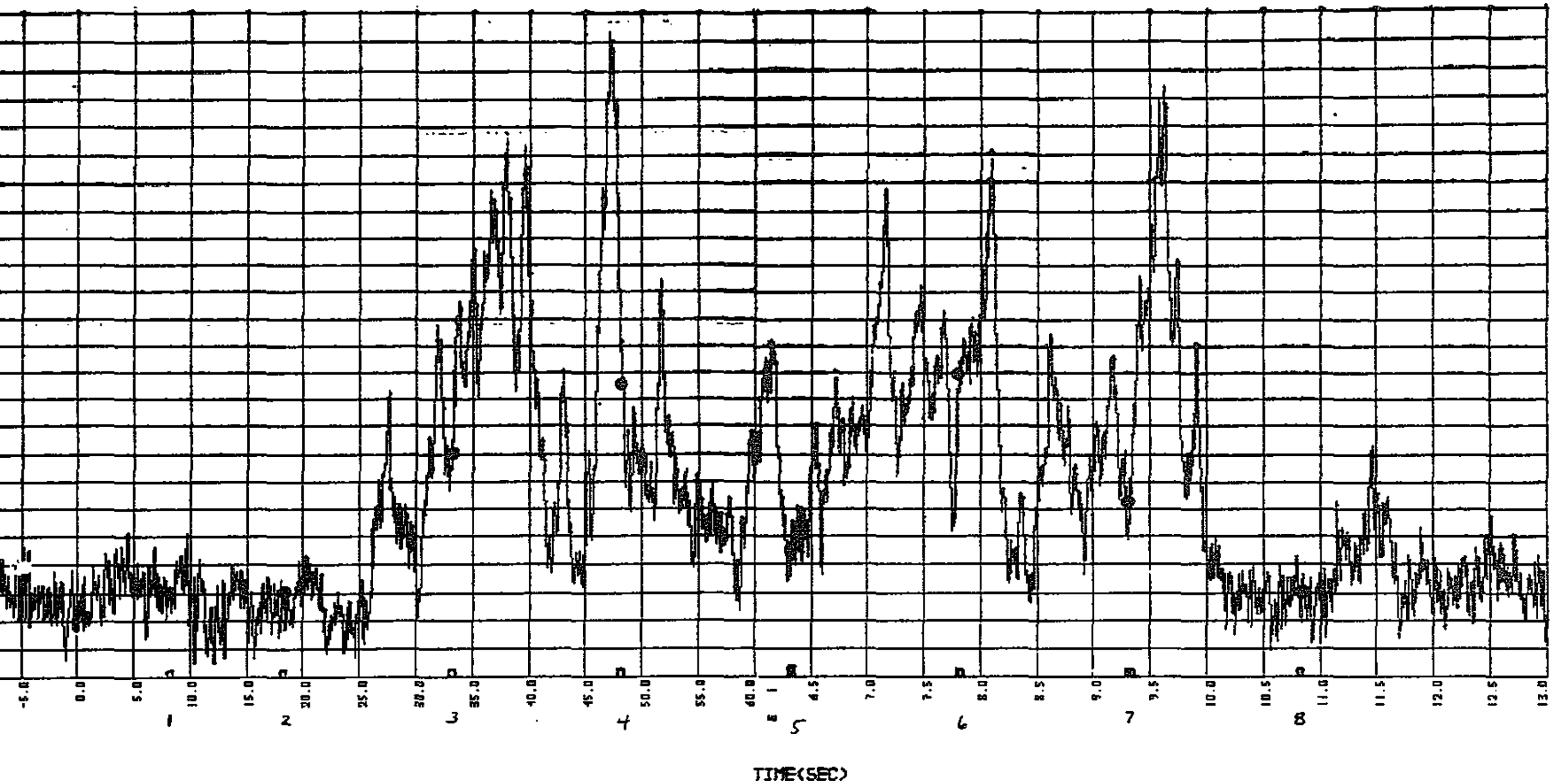
Data taken by the Shell sensor at Station 2 during our first experime
shown in Figure 8. Zero time corresponds to the opening of the spill
ve. The grab sampler measurements, which were taken for only 0.6 sec,
superimposed on the Shell data, and indicated by a small numbered squa
the time axis. The agreement between the two is excellent and we belie
at both instruments were working correctly.

The grab sampler did not happen to sample a methane concentration
ak, unfortunately. It would seem apparent from the above description
at this device should also be temperature dependent. We found in
boratory tests, however, that it was not significantly affected by gas
emperature unless the housing temperature was lowered substantially. We
ld choose to warm the gas before it got to the sensor head anyway, becau
f uncertainties about how cold the head would get during a spill and
ecause of the chance that water droplets would damage the filaments. T
as done because these sensors were used very close to the spill point,
at Stations 1 and 2.

TSI Detector

This device consists of two thin film anemometer elements in a sm
aspirated tube and is manufactured by Thermo-Systems Inc. Since this i
by design, a flow sensitive instrument, an orifice is placed down strea

LMS10
FILE(S).SHELL2C

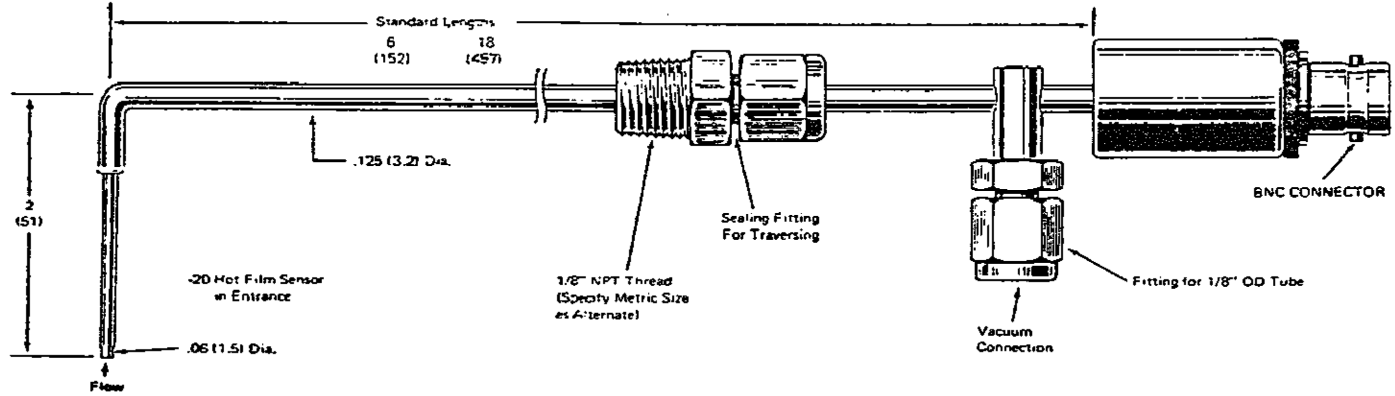


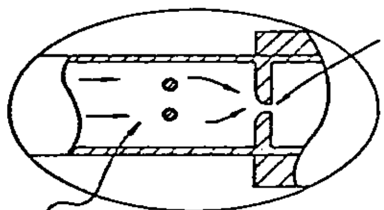
sensing elements. Sonic flow occurs at this orifice and is dependent gas composition (i.e., the sonic velocity in air is only 0.77 of that in hane). A drawing of the probe is shown in Figure 9. If the temperature nains constant, only changes in gas composition will change the velocity rough the sonic throat. This instrument is truly temperature sensitive. compensate for this, a resistance temperature probe (RTD) was incorpora to the system ahead of the aspirating probe. The output from the RTD wa electronically compensate for temperature variations in the incoming ga e range from 0° to 50°C. The response of this RTD is rather slow and th apid temperature fluctuations present in the spill environment must be emoved. Also since the thin film elements might be damaged by the water roplets present in the LNG vapor cloud, the gas was drawn through copper ubing coils in a water bath which warmed it to ambient temperature and vaporized the water droplets.

The second element inside the probe was unheated and used as a temperature measuring device. Output from this element showed that the temperature fluctuations present in the LNG vapor cloud had been removed the gas stream and that only a very gradual increase in temperature, of than 1°C, was observed during the course of the experiments.

Calibration of the systems showed that the TSI output was very li with methane concentration over almost the entire 0% to 100% range. Th was not flow rate dependent and temperature changes were eliminated by warming the gas. A complete calibration was performed before the senso were installed and calibration checks were performed throughout the ex series. There was no significant change in calibration during this ti

Model 1441 Aspirating Probe – 90° Angle





nsors are fragile and several were broken prior to being installed in t
. Once installed, however, they performed well and were left essentiall
ched during the entire experimental series.

The response of the instrument alone is very fast, about 10 ms. The
l was filtered at 100 Hz to preserve this response. Unfortunately, thi
allowed a lot of noise (mostly 60 Hz) to propagate through the system.
ple of the TSI output, from the 8 foot level of station 3 for LNG-18
et 1) is shown in Figure 10. Also shown in this figure are the grab
le results (0.6 sec sample time). The agreement between the grab sampl
lts and the sensor output is quite good. The fastest rising (or fallin
ctuations observable in this data have a frequency of about 5 Hz. Hence
100 Hz frequency response is probably unnecessary and the output could
efit from some smoothing or filtering without any real loss of informat
moothed version of the same data is shown in Figure 11. Most of the
se has been eliminated, but any high frequency concentration fluctuatio
sked by the noise, have also been eliminated.

arad IR Detector

This is a non-dispersive, infrared gas analyzer custom built for us
Anarad Incorporated of Santa Barbara, California, to measure methane,
thane, and propane in the presence of air and water vapor. The system w
eally three analyzers, one for each of the hydrocarbon species of inter
schematic drawing of one of these units is shown in Figure 12 and a
icture of the complete instrument in the field at China Lake is shown i
Figure 4c. The detector chamber for each channel of the system was fil
with a mixture of the other two gases which acted as a negative filter.

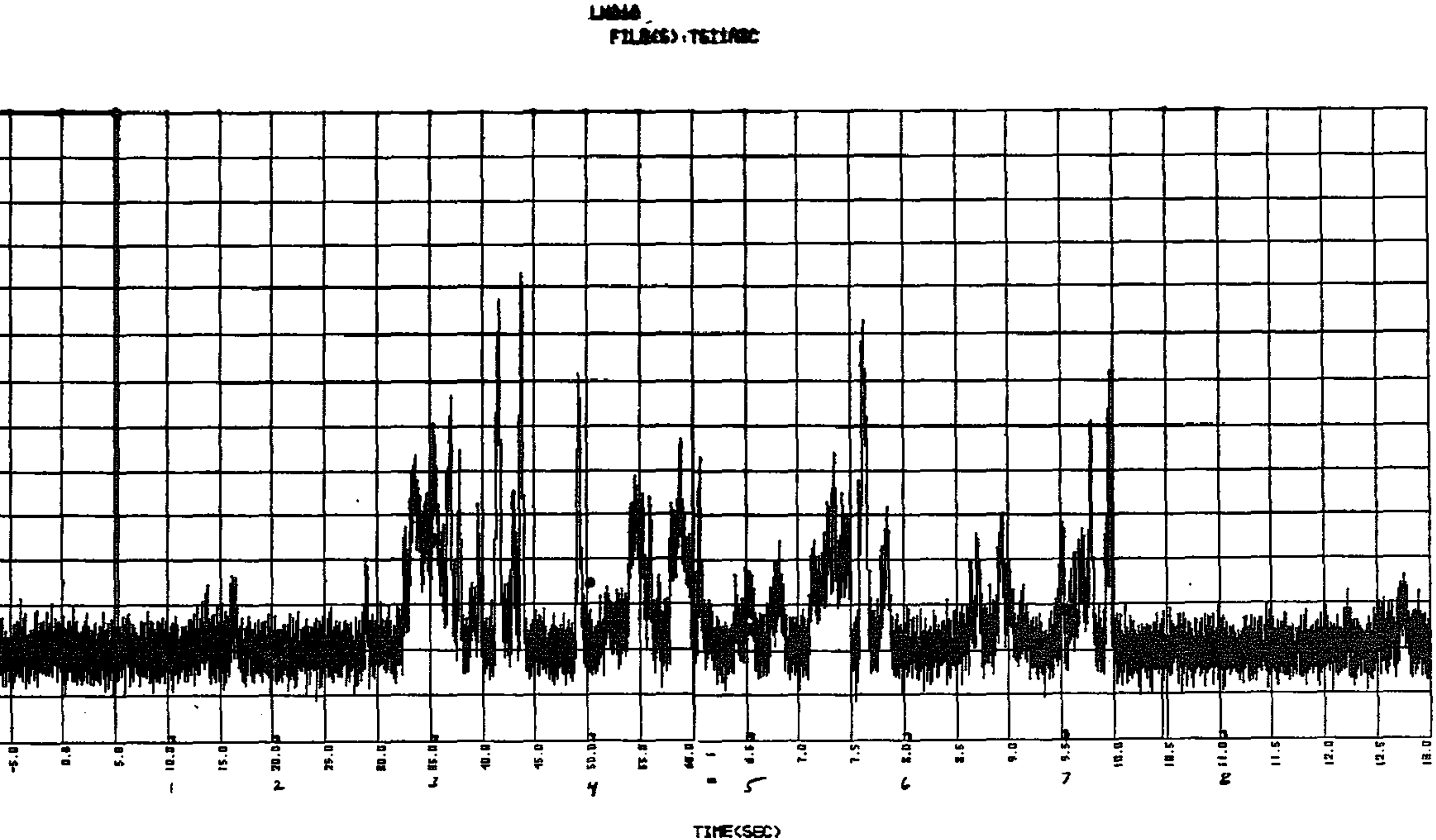


Figure 10. TSI output from Avocet 1 (LNG18) for the 8 foot level

LNG18
FILE(S):TSI1R3C28

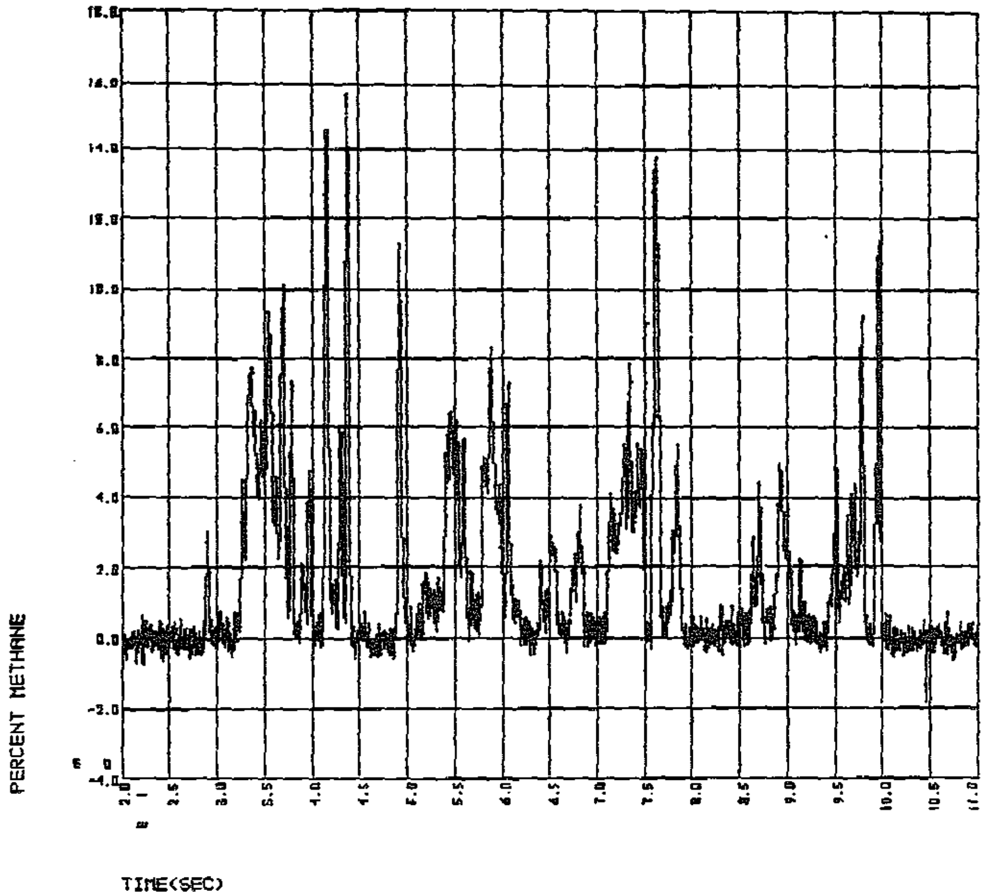
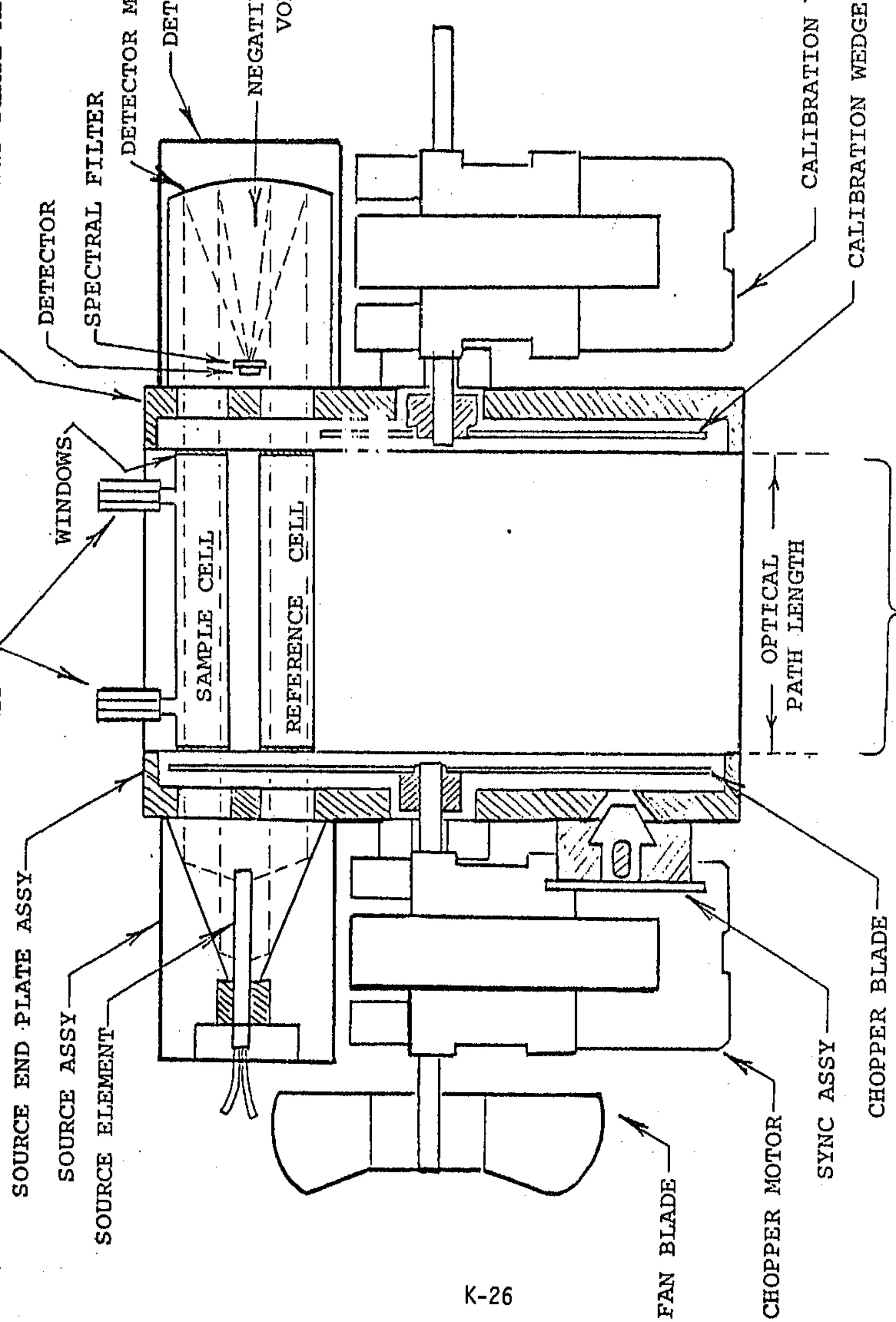
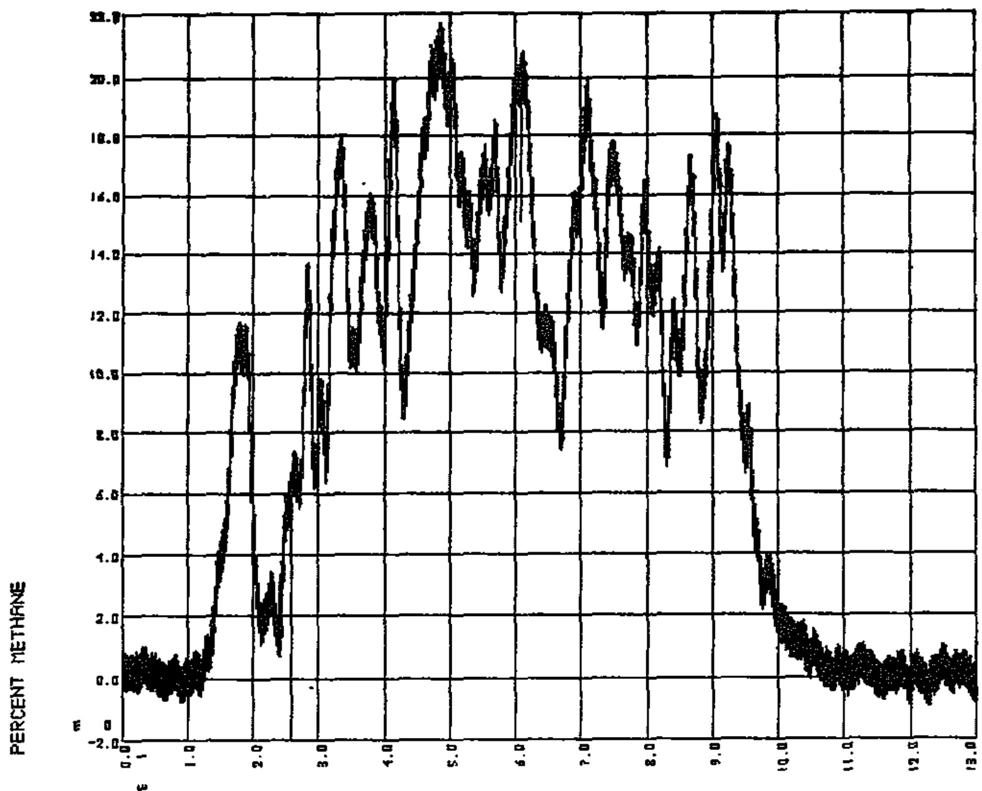


FIGURE 11 Smoothed TSI data from Station 3, LNG18.


DETECTOR
SPECTRAL FILTER
CALIBRATION WEDGE
WINDOWS
SAMPLE CELL
REFERENCE CELL
OPTICAL PATH LENGTH
SOURCE END PLATE ASSY
SOURCE ASSY
SOURCE ELEMENT
FAN BLADE
CHOPPER MOTOR
SYNC ASSY
CHOPPER BLADE

eference cell contained air and was illuminated by the same IR source a
luminated the gas/air mixture flowing through the sample cell. Filter
ere used to further select the spectral region characteristic of each g
here was still some residual cross-talk between the channels, however,
attempt was made by Anarad to remove this electronically. This was c
rginally successful in that the compensation circuitry left large tran
ent spikes in the output of some of the other channels. By changing
pacitors in the compensation circuitry, we were able to bring these sp
wn to 7% in the methane channel and 1.7% in the propane channel. Data
om this instrument, before the capacitor changes were made, is shown i
gures 13, 14 and 15. In addition to the transient spikes mentioned
ove, there was a certain amount of constant cross talk present. A 100
thane step input produced a 3.5% ethane step response and a 0.6% propa
ike. A 7.6% propane step input produced a 2% methane step response.
e data shown in Figures 13, 14 and 15, one can expect uncertainties to
e extent of about 1% in certain regions of the methane data, uncertain
about 0.7% in certain regions the ethane data, and uncertainties of a
5% in certain regions of the propane data. Those uncertainties associ
th constant cross-talk will be corrected before the data are published
ose uncertainties associated with transient cross-talk due to rapid
ncentration changes are difficult to correct and will simply be errors
e measurement.

LNG19
FILE(S): IR4-MC



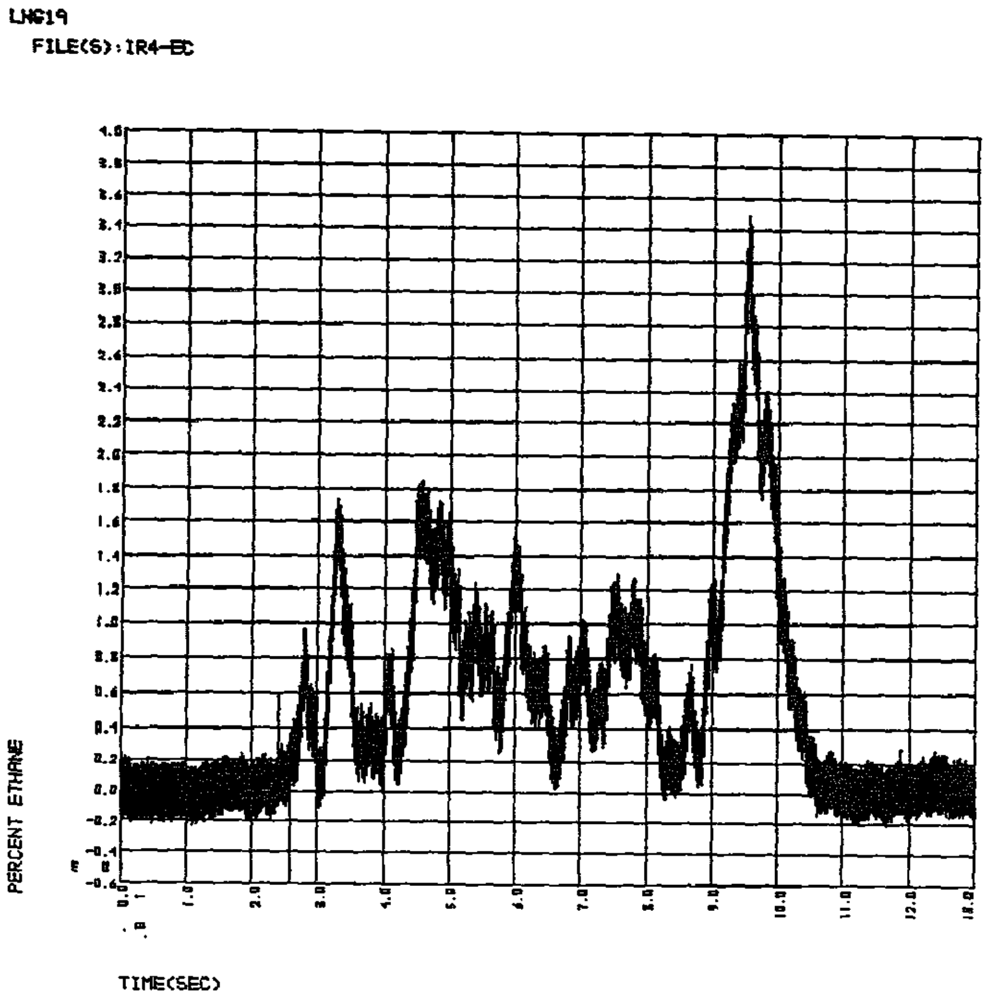


FIGURE 14 Ethane concentration from the Anarad IR detector

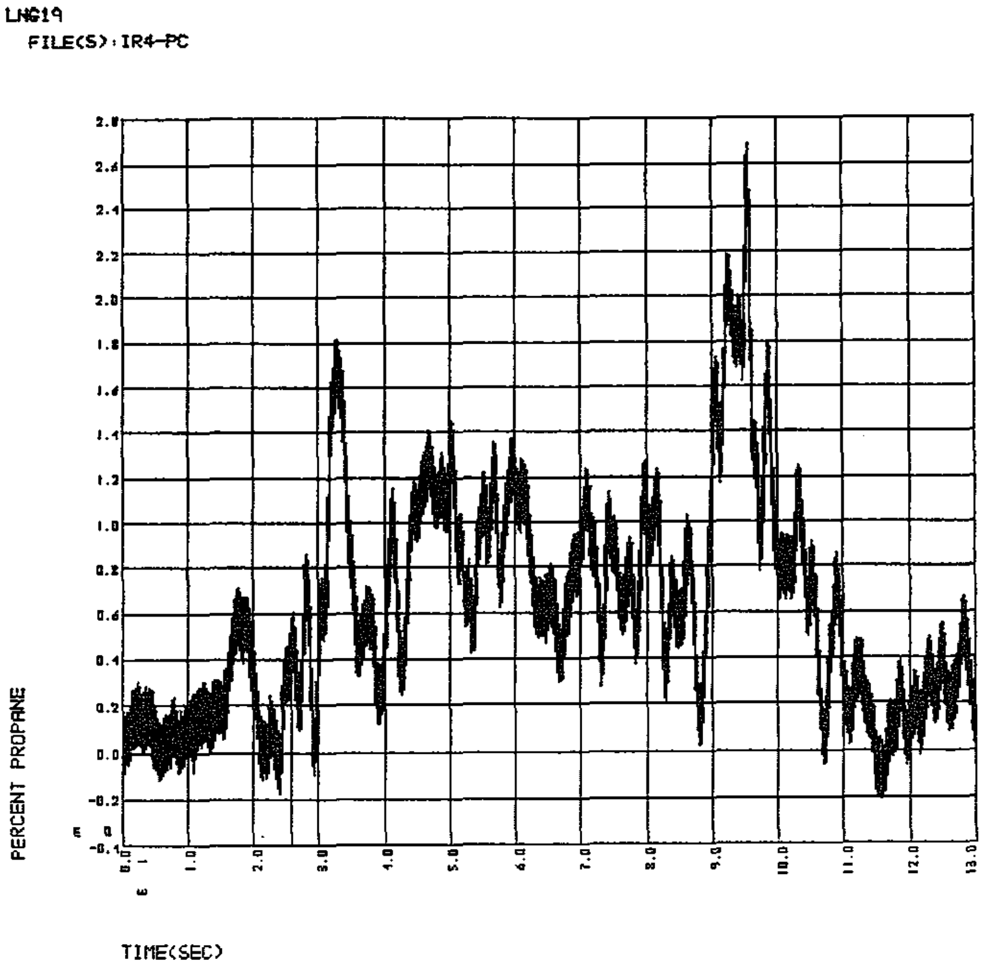


FIGURE 15 Propane concentration from the Anarad IR detector at

The response time of the instrument was several seconds, subst more than the 0.1 - 0.5 sec response anticipated. It may be possibl decrease this response time by increasing the flow rate through the cell but we suspect that a major system redesign would be required f to be a good field instrument.

LLL IR Detector

The LNG Program has been fortunate to have had the use of a mi rapid-response infrared detector prototype developed for the DOE CO_2 A drawing of the sensor optical bench is shown in Figure 16 and a picture of the unit in the field at China Lake is shown in Figure 17 prototype was modified only to the extent that it can detect hydroca (methane, ethane, and propane) in the presence of air and water vapo droplets) rather than CO_2, because of the short time available. Thi modification consisted of replacing the CO_2 filters with a 3.85 μm r filter and 3.268 μm methane filter. The filters were chosen to indi as methane. No effort was made to discriminate among the various hy

The sensor operates on the principle of differential absorptio one of the filters centered on a methane line and the reference filt centered nearby on a background region. The ratio of these two meas is then essentially independent of water vapor, water droplets, or d the absorption cell. The sensor has a full scale response of 10 Hz operates non-thermostated in environments with temperatures from -20 +40°C.

The sensor uses a microprocessor, a feature which we believe w permit the interference free detection of methane, ethane, and propa

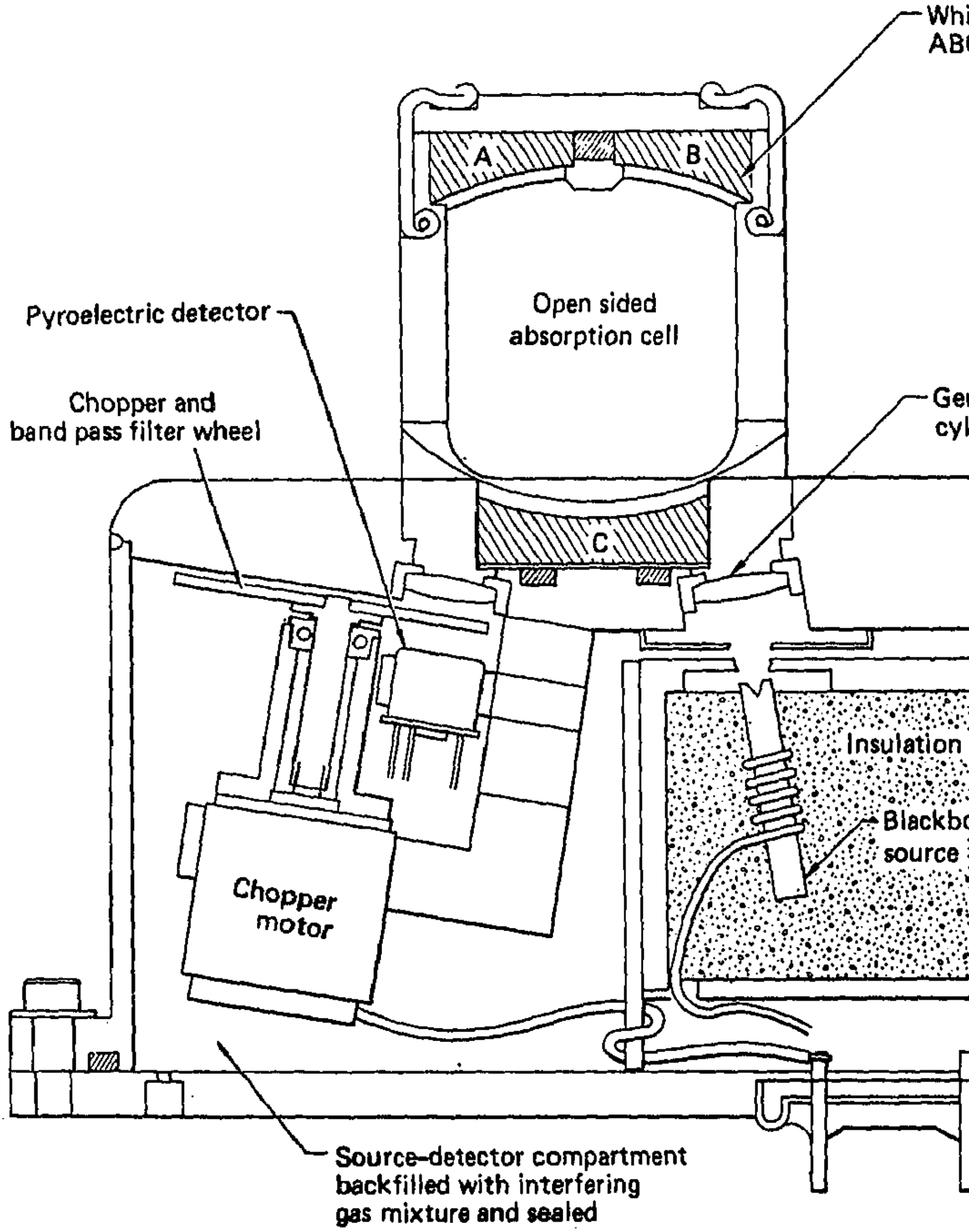
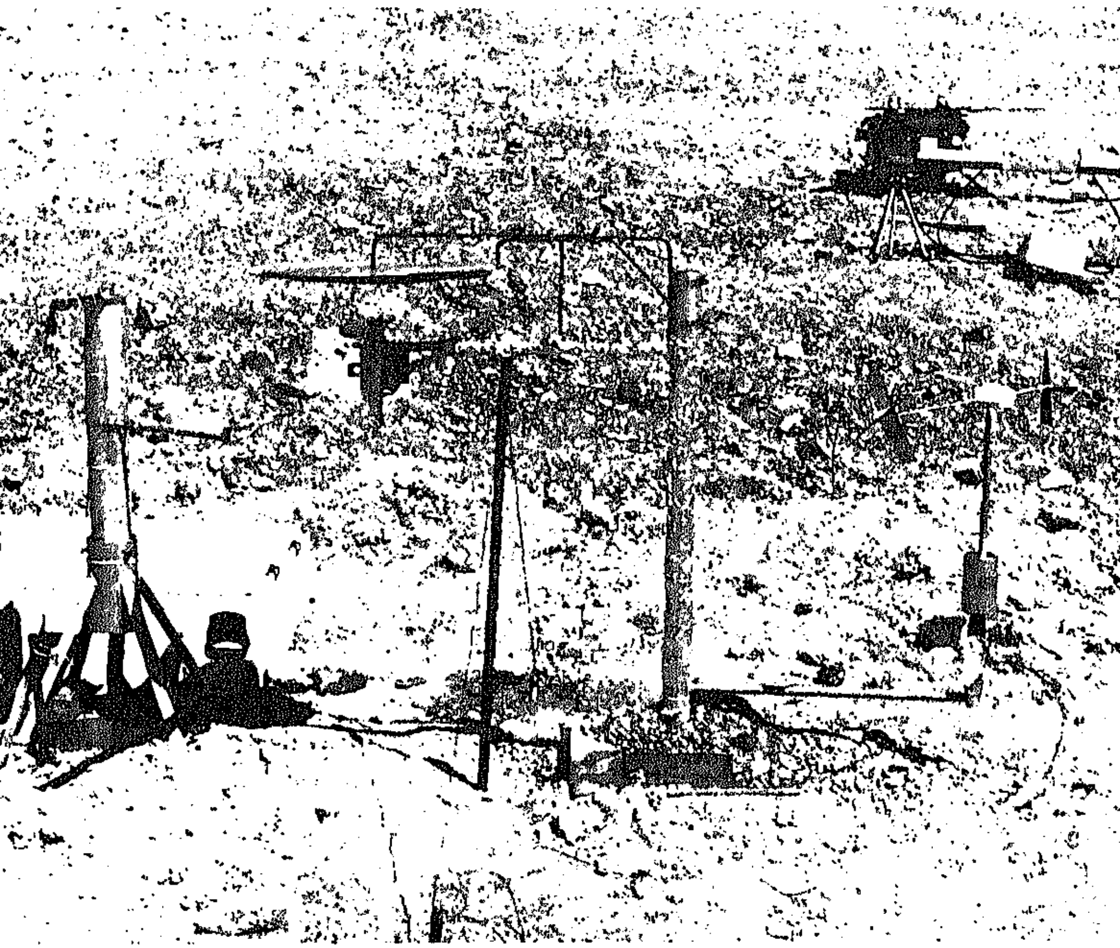


FIGURE 16 The Optical Unit of the LLL Designed Miniatu
Rapid-Response Infrared Detector



IGURE 17 The LLL Infrared Sensor at Station 5

his would involve incorporating five filters on the filter wheel instead f two and using matrix algebra and the microprocessor to make the necessa ross talk corrections. In addition, this sensor is the only truly portab nvironmental sensor evaluated during the tests. The measuring volume is mall and open to the atmosphere so that pumps and water baths are not equired. The optical bench is light weight (1 kg) and is separate from lectronics package, allowing easy incorporation on inexpensive and portab owers. The electronics package is also small (2000 cm^3) and contains ufficient battery power for a four hour test. Data storage can also be rovided within the electronics package.

Data taken with this sensor at Station 5 on LNG21 is shown in Figure 18. Also plotted on the figure are the grab sample data from Station 5. he agreement is fairly good and not inconsistent with that observed for ther sensors. Grab sample 4 (at 67 sec) was a short sample (0.6 sec) and ndicates that the sensor response may not have been fast enough to follo hat appears to be a sharp dip in gas concentration at about that time. R detector and the grab sampler intake were separated by about two feet, hich may also account for some of the differences between the two instru

MSA Detectors

The MSA gas sensor is designed as a passive instrument for the dete tion of flammable gases and vapors up to their Lower Flammability Limit (in air. The sensor head contains a pair of heated filaments which are pa of an electrically balanced bridge circuit. One element is catalyst coat and combusts the flammable gas while the other is inert and responds only

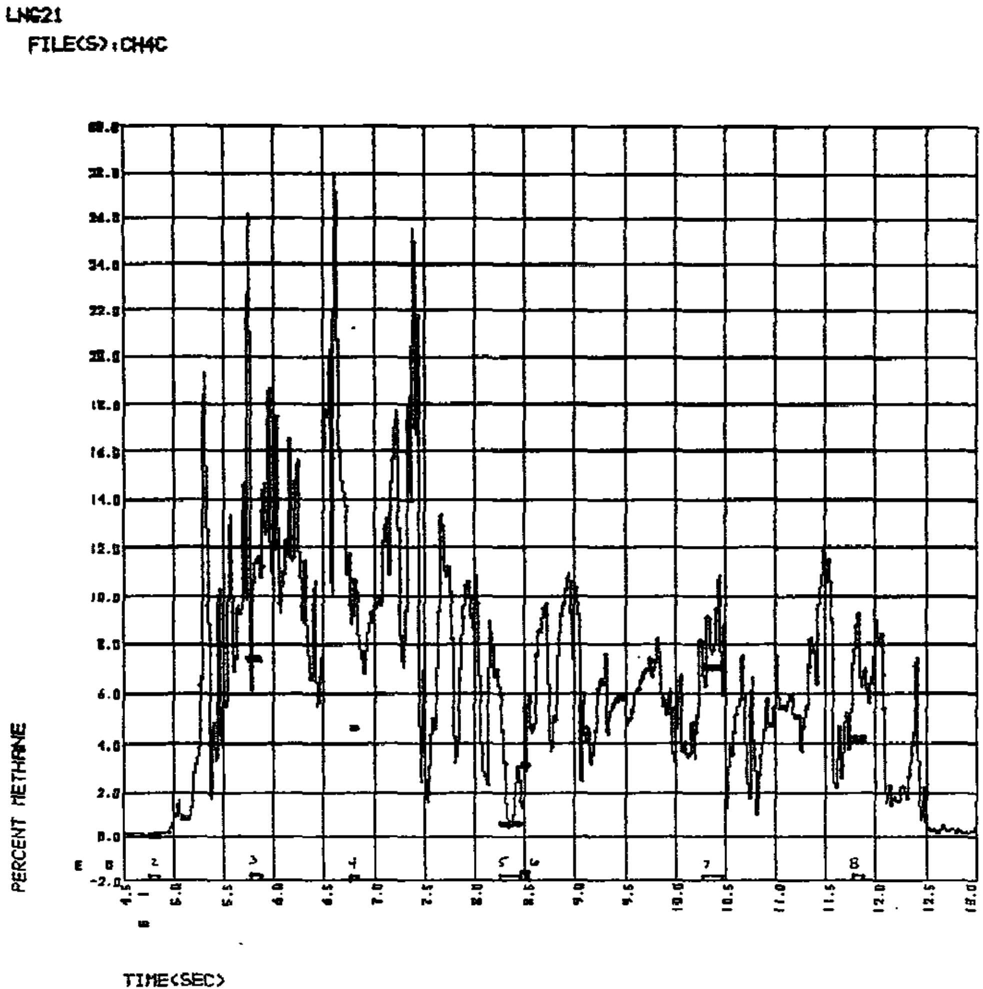
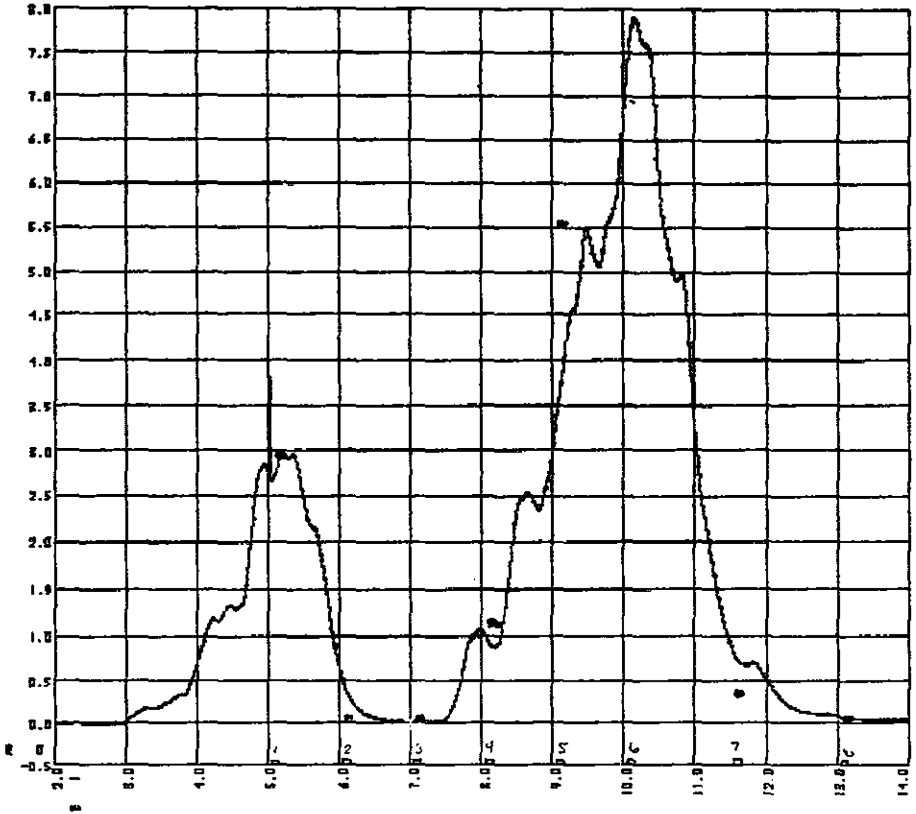


FIGURE 18 Data from the LLL infrared sensor at Station 5 for LNG21

to the ambient temperature, humidity, and pressure changes. This ten to compensate for these same effects on the catalytic filament. We d find that this was not entirely successful, however, and that the instrument was sensitive to strong winds. The gas being monitored is past the filaments by diffusion through the sintered stainless steel arrestor and by the natural draft caused by the heated elements. Whe flammable gas contacts the catalytic element it combusts, increasing temperature of the element and changing its resistance which unbalanc bridge curcuit. A picture of the sensor head at Station 7 is shown i Figure 3d. Data taken with this detector at Station 8 on LNG19 are s in Figure 19. Also shown on this figure are the grab sample results this experiment. It is apparent that the grab sample results agree v well with the MSA data if about 3 seconds are added to the grab sampl times. Since a delay of nearly 2 seconds is already included in the sample timing this indicates a time delay of about 5 seconds for the MSA detector which is consistent with what has been observed by other Since the MSA sensor relies on combustion of the gas for its signal, output increases only up to stoichiometric gas concentrations i.e., 1 the concentration exceeds 10% the sensor output decreases. We observ the output was nearly 2 volts at 10%. It should be noted that the in is advertised as only being able to detect gas concentrations up to t (5%) for which the output is about 1 volt.

LWG19
FILE(S): MSABC



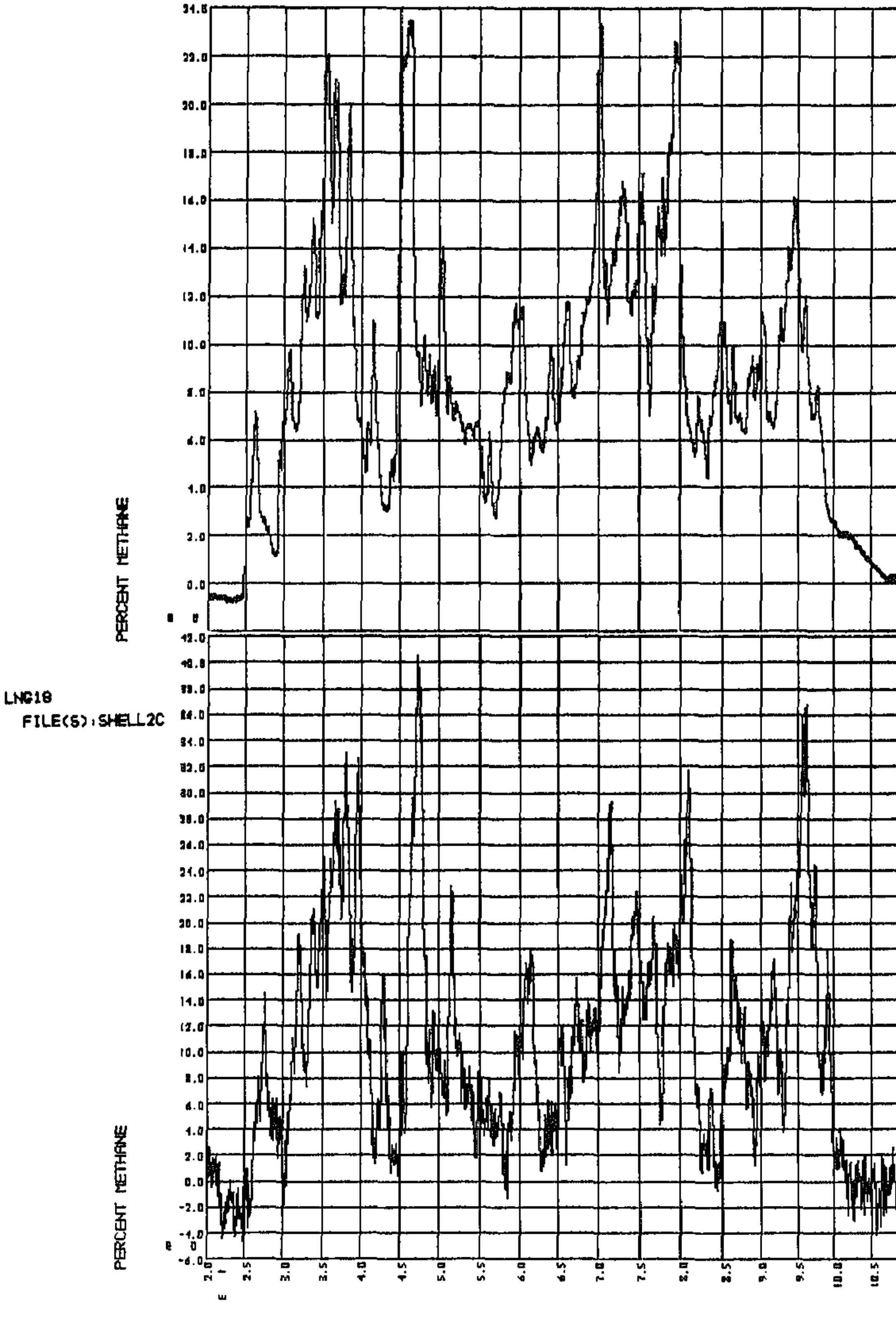
Thermocouples

Two chromel-Alumel, Inconel sheathed, thermocouples were mounted each sampling location. These locations are shown in Figure 2 for the experiments. For the first two experiments, the thermocouples only ext to 8 feet. The results of these measurements indicate that though most cloud stays low, we do see parts of it even at 15 feet.

The thermocouples were relatively fast response (listed at 0.1 se 0.010 inch diameter devices which were fitted with solar shields. In c experiments the effective response time of the thermocouples was signif more than 0.1 sec, more of the order of 0.5 sec. A photograph of an in tion at a sampling inlet is shown in Figure 4b. The thermocouple outpu amplified in the associated station and transmitted to the recording tr on long cables.

Equilibrium thermodynamic calculations were performed, including mixing with ambient air and the condensing and freezing of water. Thes were then used to relate the gas cloud temperature to the concentration methane. Figure 20 is a comparison of the methane concentration measur by the Shell sensor at Station 2 on our first experiment (LNG-18) with inferred from the temperature measured by the thermocouple at the same station. First, the 1.8 sec difference in timing caused by drawing the sensor sample through the coil of tubing is quite apparent. Second, th correlation in time and in relative intensity of peaks between the two sensors is quite remarkable. The temperature excursions correspond to concentration excursions just as expected. Third, however, significan

FILE(S):TC1A2T



differences in indicated concentration exist between the Shell and couples. The thermocouple implied concentration is only 60% of tha by the shell sensor. This is probably due to non-equilibrium effec sources of heat not included in the calculation.

Anemometers

Anemometers were installed at Station 4 (later moved out over to Station 2), Station 5, and halfway between Stations 6 and 8. Th installed about 3 feet above the ground and were used to monitor th air flow during the course of the experiment. In addition to these had two anemometers installed on a meteorological tower to the sout of the spill pond at the 2m and 10m levels.

The anemometers used for these experiments were of the bivane which are preferred for turbulance work very close to the ground be provide information on all three components of the wind at a single They have a distance constant (wind passage for recovery from a ste in speed or direction) of about one meter and a threshold of about 0.1 - 0.2 m/s.

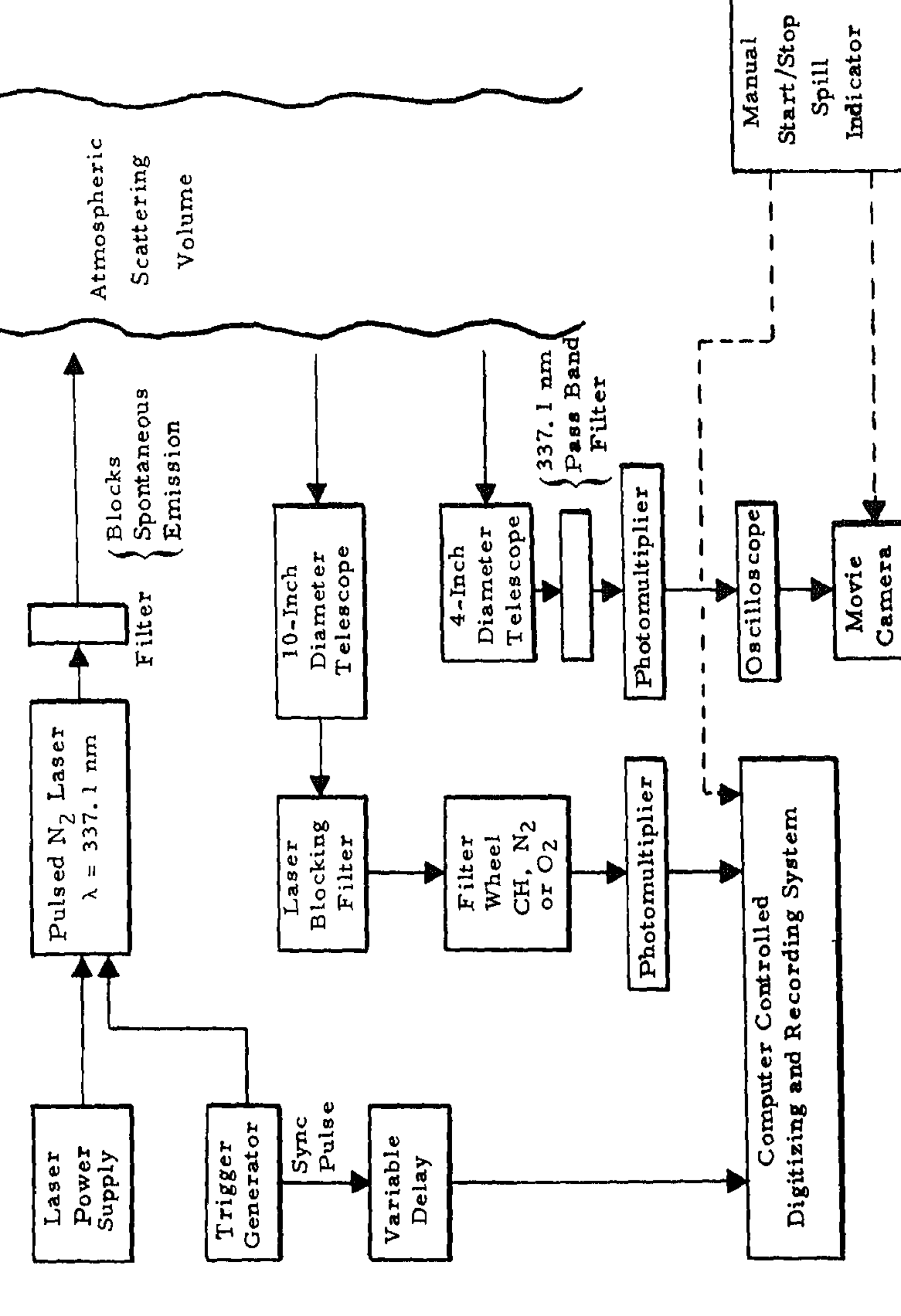
Anemometry data were recorded for at least 5 minutes before a the spill experiments. A summary of the anemometry data recorded du the experiments is given in Table 1. These values were obtained fro averages over periods when the wind direction was relatively consta appears from the data that the wind direction and speed vary consid from place to place on the spill site.

The CGC LIDAR

Gas concentration can be determined remotely by using a laser to measure either the optical absorption of the cloud, or the emission of frequency-shifted Raman component. Of the two techniques, the Raman sy holds the most promise for LNG diagnostics, and was, therefore, tested China Lake. The goals of the test were to determine the feasibility of using a remote measuring system, and the limits that the cryogenically- produced fog would impose on the region of the cloud that could be meas

The construction of even a simple LIDAR system requires a signifi investment of time and effort. Therefore, a contract was given to Comp Genetics Corporation (CGC) to field their existing instrumentation and mobile van to measure total hydrocarbons at eight range gated positions across the vapor cloud. The CGC Raman system did not incorporate a scanning capability, nor were the optics and laser power adequate for t high time resolution that a scanning system would require. Also, the t to be performed at night because of the large laser divergence and tele acceptance angles. These limitations could, however, be eliminated in future, and the system provided an adequate test of the usefulness of a remote measuring system. A block diagram of the CGC LIDAR system is sh in Figure 21.

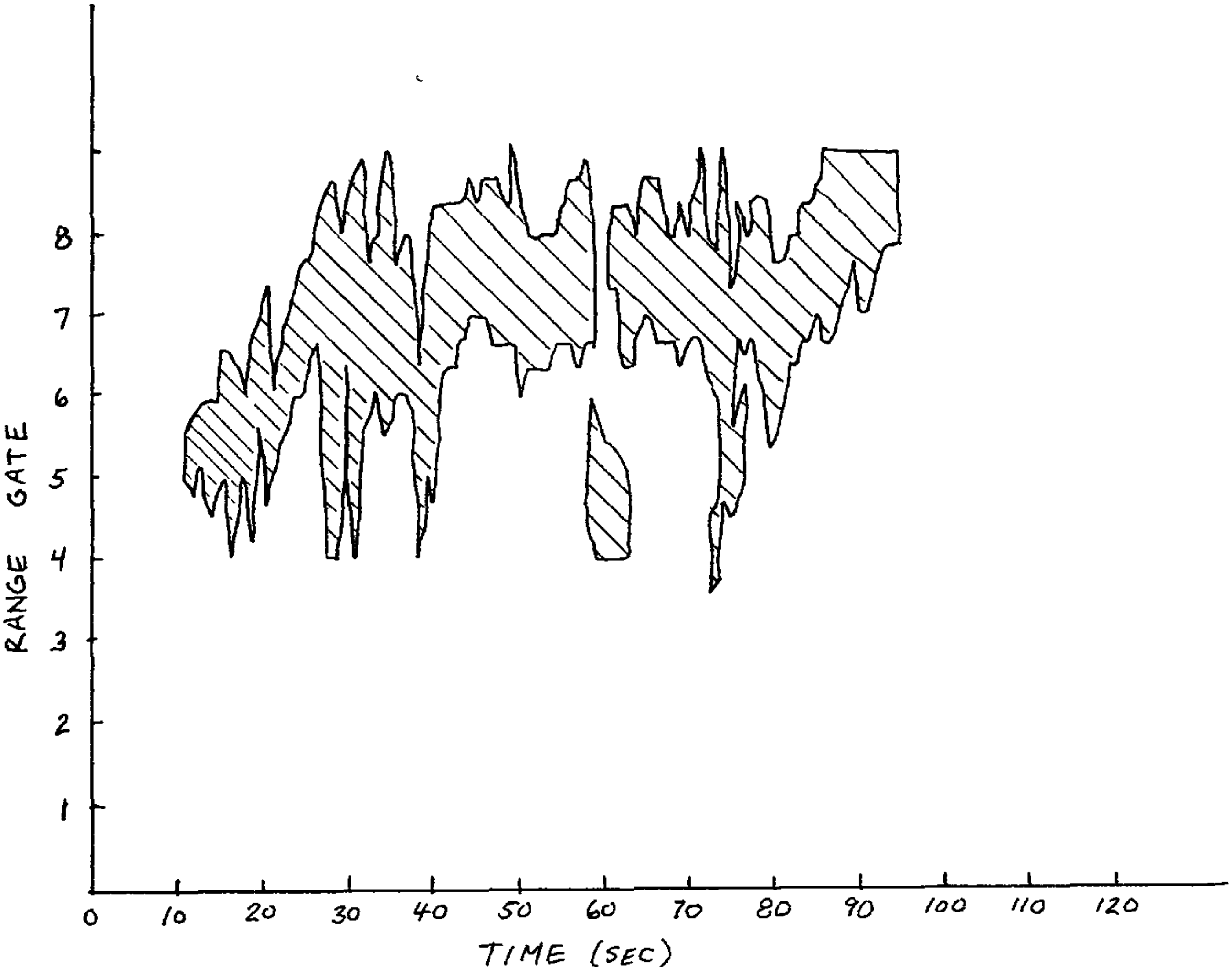
The LIDAR van, with N_2 laser and receiving telescope, was situate relative to the pond as shown in Figure 1. In the vicinity of the pond, the laser beam was two feet above the ground (seven or eight fee above the water level). The total path length from the van to a reflec across the pond was 450 feet. The laser emitted pulses of 10 ns durati

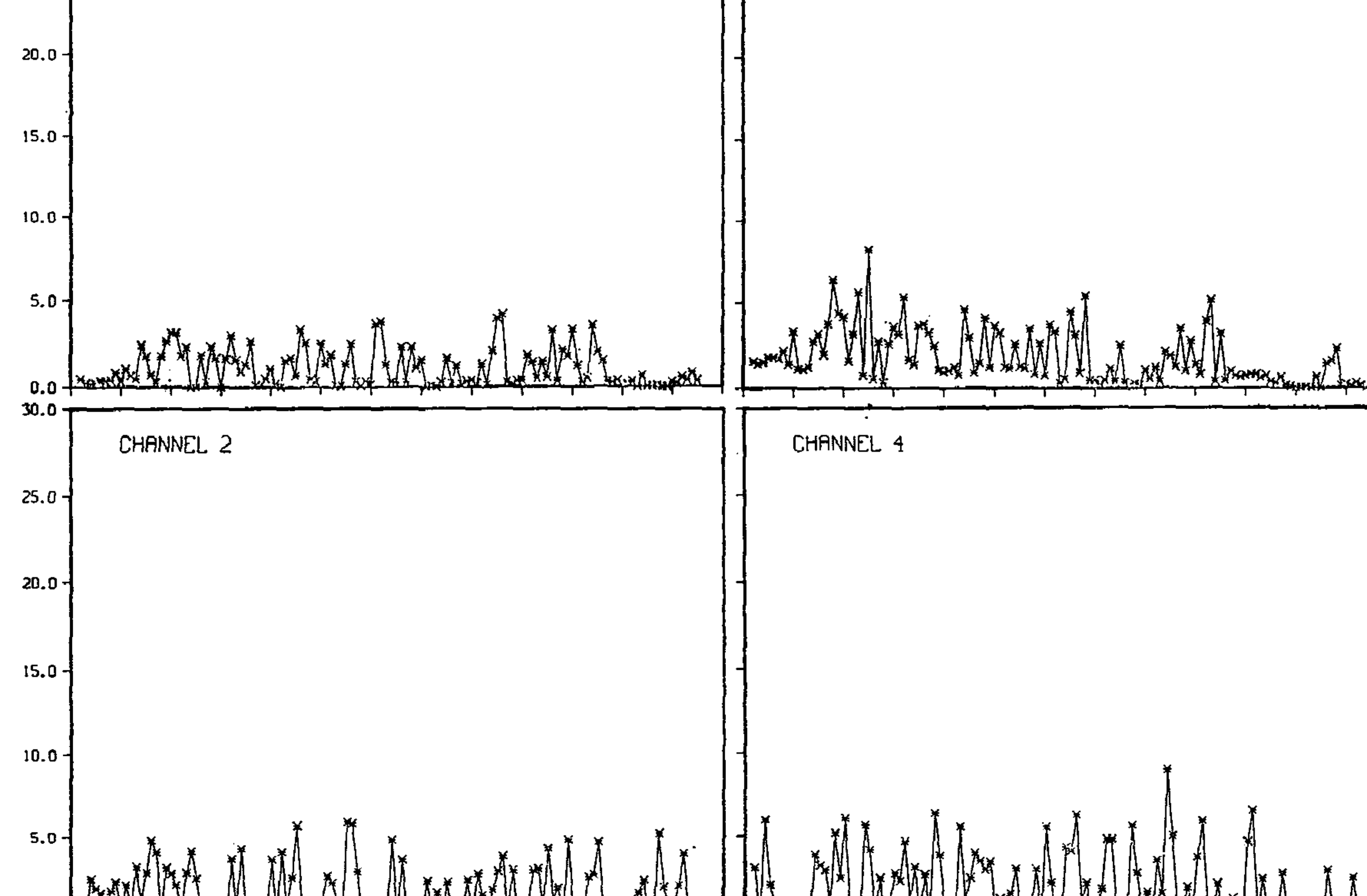

Atmospheric Scattering Volume
Blocks Spontaneous Emission
Filter
Pulsed N_2 Laser $\lambda = 337.1$ nm
Laser Power Supply
Trigger Generator
Sync Pulse
Variable Delay
10-Inch Diameter Telescope
Laser Blocking Filter
Filter Wheel CH, N_2 or O_2
Photomultiplier
4-Inch Diameter Telescope
337.1 nm Pass Band Filter
Photomultiplier
Oscilloscope
Movie Camera
Manual Start/Stop Spill Indicator
Computer Controlled Digitizing and Recording System

(10 feet spatially). The Raman scattered light was gated to produce return signals per laser pulse, corresponding to the eight 30-foot r shown on the figure. The signals were digitized and recorded in a c memory for later analysis. The presence of fog in the laser path wa monitored by recording on an oscilloscope an elastically backscatter component of the laser light.

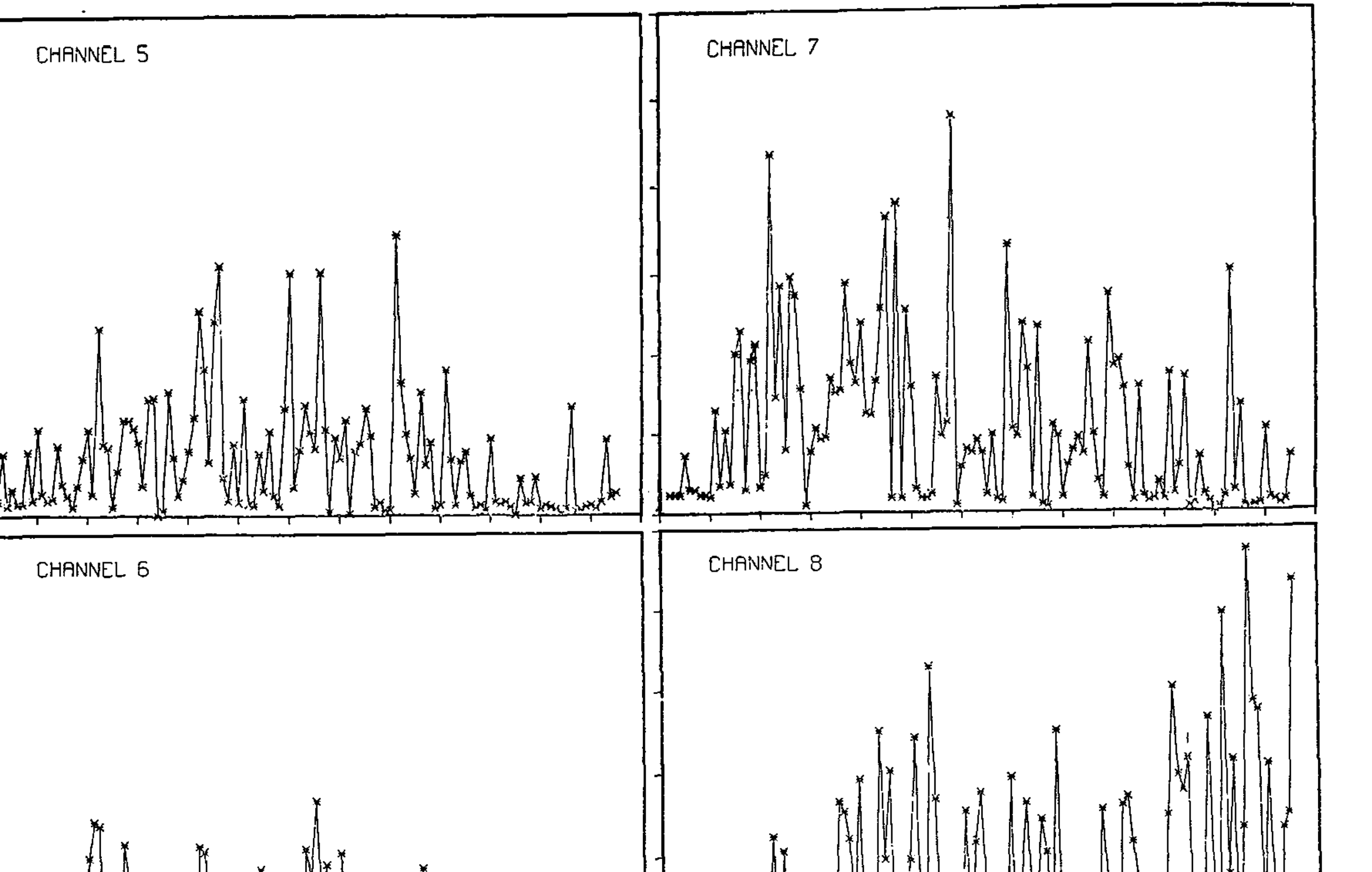
At present we have only preliminary data from CGC. Many concl *should be qualitatively correct. However, quantitative conclusions* regarded as being tentative. The position of the fog as a function after the spill is indicated in Figure 22. (The width of the cloud exaggerated to some extent by the limitations of the film reading pr During most of the time, the fog allows essentially no direct penetr Raman signals from behind the cloud are to be expected, but they are longer from a direct laser-to-reflector path, and measured concentra will, therefore, be of uncertain location.

Concentration data are shown for each range gate in Figures 23 24. It is interesting to find that flammable mixtures extend all th to the edge of the pond, 120° relative to the spill point from the w direction. Also interesting are the sharp fluctuations in concentra which were probably caused primarily by vertical turbulence. Examin range gates that are just ahead of the fog, we find that concentrati seldom exceed 6%. Considering that these results are from averagin *one second intervals, and over a spatial volume of about 30 ft^3, thi* quite reasonable agreement with the approximately 10% peak concentra that would be expected under the temperature and humidity conditions the time of the spill.


RANGE GATE
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME (SEC)



20.0
15.0
10.0
5.0
0.0
30.0
25.0
20.0
15.0
10.0
5.0
CHANNEL 2
CHANNEL 4


CHANNEL 5
CHANNEL 7
CHANNEL 6
CHANNEL 8

No detailed comparison of in situ and LIDAR data can be made due
spatial averaging nature of the LIDAR, and to the six foot depression o
pond, which prevented the laser beam from being located near the vertic
position of most of the in situ sensors. Average concentrations from t
LIDAR are about 1/3 those of nearby, but lower in situ instruments (ran
gate 5 vs Stations 1 and 3, and range gate 6 vs Stations 2 and 4). Thi
consistent with the height distribution of the one relevant in situ sta
(no. 3, with sensors at 5 feet and 10 feet above the pond level).

Given the variable desert conditions of future spills, LIDAR shou
be usable at concentration levels from below 1% up to 10 or 15%. It wi
not see into or through the fog associated with the central high concen
tion region. But it will map out a majority of the cloud in regions of
flammable concentrations. LIDAR should be useful, and cost effective
when employed in conjunction with a course grid of in situ instruments
large (100 to 1000 m^3) spill tests.

ACKNOWLEDGMENT

We wish to thank Shell Research Limited (Thornton Research Center
Chester CH1 35H, UK) for the extended loan of a methane sensor used in
these evaluation studies.

REPORT L

China Lake Spill Tests

C. D. Lind
J. C. Whitson

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Naval Weapons Center
China Lake, California 93555

REPORT L

TABLE OF CONTENTS

TABLES

This report describes spill tests and instrumentation assessment by the Naval Weapons Center at China Lake. This report covers LNG te through 21, conducted between May 25 and November 20, 1978. The spil ments yielded an extensive amount of data on instrumentation techniqu combustion and dispersion characteristics, which are still being anal Details of the meteorological, photographic, radiometric and concentr monitoring instrumentation used in these tests are discussed and exam radiometer and vapor concentration records are presented.

INTRODUCTION

For the past 6 years the Naval Weapons Center has been investigating the fire and explosion hazards of liquefied fuels[1,2]. This work was supported originally by the U.S. Coast Guard and more recently also by the Department of Energy, Division of Environmental Control Technology. During this program a facility was constructed for spilling liquefied fuels onto a water pond and studying the combustion or dispersion of the resulting vapor. The facility has been used to conduct 21 spills of liquefied natural gas (LNG), 8 spills of liquefied petroleum gas (LPG), one spill of gasoline and one spill of liquid nitrogen. This report covers LNG tests 12 through 21 inclusive, performed during the period 25 May-20 November 1978. The tests were funded by the Department of Energy and the U.S. Coast Guard (with funds from the Gas Research Institute).

The object of tests LNG 12, 13, and 14 was to obtain radiometric measurements to determine if the flames observed were optically thick (that is, had reached a diameter such that increased flame thickness did not result in increased radiation from a unit area of flame). Test LNG 12 was an immediate ignition pool fire. Tests LNG 13 and 14 were delayed ignition pool fires. For these, ignition was delayed in order to produce a maximum diameter flame.

Tests LNG 15, 16, and 17 were downwind vapor ignition tests, performed to obtain vapor combustion characteristics and radiometric measurements to compare with the pool fire measurements. Unfortunately the wind shifted during test LNG 15, dispersing the LNG vapor away from the ignition flares, and no ignition occurred.

Tests LNG 18 to 21 were performed to determine downwind vapor dispersion characteristics and to evaluate concentration monitoring instrumentation. Ignition was not planned (and none occurred). Test LNG 19 was performed after dark to evaluate an instrument that was adversely affected by daylight (Raman LIDAR). Photographic coverage was obtained for all tests except LNG 19.

AREA DESCRIPTION

The CT-6 test site location is shown on Figure 1. The site is located in the southeastern portion of the Naval Weapons Center China Lake complex, in an area called the Salt Wells Valley. The test facility is located on the northern edge of a relict river channel in an area that has developed into a small playa. The site is isolated, being 2.2-km from the Center's southern boundary and 1.3-km from the nearest building. The terrain is generally flat with a maximum elevation change of 70-m within 2-km.

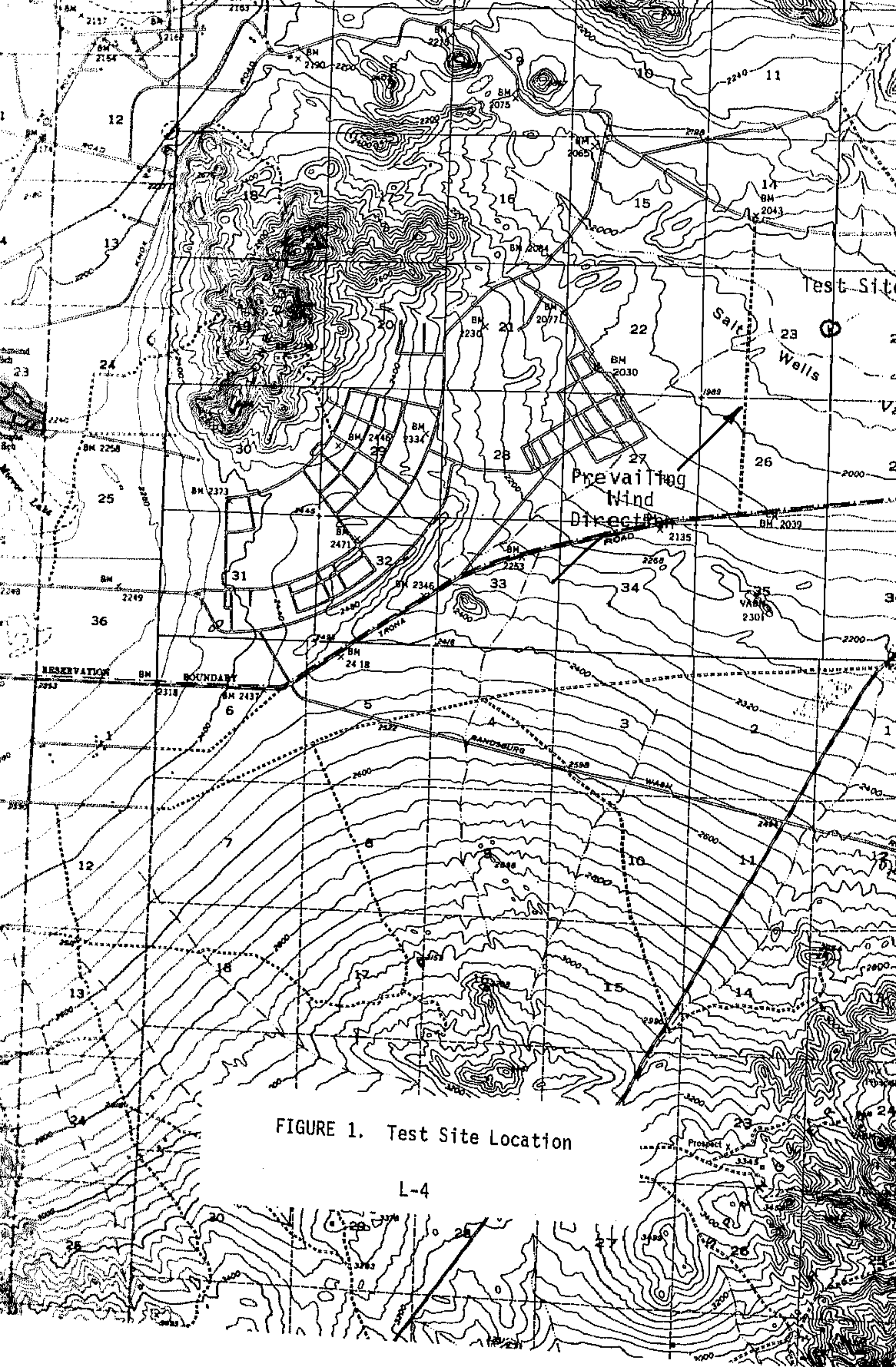

FIGURE 1. Test Site Location

The general arrangement and terrain of the test site is show
Figure 2. The features of the site used for the spill tests are
spill equipment on the south side of the pond, the pond itself,
the control bunker 200-m northwest of the pond. The pond is app
imately 50-m square and 1-m deep. The water is brackish natural
ground water.

SPILL FACILITY

The spill equipment consists of a holding tank, a pressuriza system, a vent system, a spill line, and associated controls and instrumentation. The holding tank is an 8-m^3 stainless steel ta insulated with 200-mm - thick closed cell polyurethane foam. I not vacuum jacketed. The evaporation rate of LNG from the vente tank has been found to be approximately 0.7-m^3/day.

During loading and standby the boil-off is vented to the atm sphere through vent valves to a 5-m high vent stack. The pressu ization system consists of a gaseous nitrogen supply trailer, co taining nitrogen at 125 bar pressure, and two-stage pressure re- duction valves to reduce the nitrogen pressure to 3-6 bar pressu (nominal). The spill line is a 150-mm pipe extending from the holding tank to the center of the pond. It has a main spill val and a cool down valve.

Remote controls are provided for operating the vent system, pressurization system, and the spill valves. In addition, there remote monitoring of the temperature of the holding tank and spi line, of the pressure of nitrogen supply and holding tank, and o liquid level in the holding tank.

In preparation for a spill test, the holding tank is filled a tank truck, the liquid is sampled for analysis, and the pressu reduction valves are adjusted. The area is then cleared of pers and subsequent steps are done remotely. The vent valve is close the holding tank is pressurized. The spill line is cooled by al ing a small amount of the liquid to run down the spill line. Wh the spill line has been cooled, the spill valve is opened and th conducted. Normally approximately 1-m^3 of liquid is retained in holding tank to keep it cool for the next text.

METEOROLOGICAL INSTRUMENTATION

A weather monitoring station is located as shown on Figure For tests LNG 12 through 17 inclusive, the station consisted of Aerovane-type wind sensor (2-m above ground level) and a standar meteorological enclosure containing a barograph, thermograph, an hygrograph. For tests LNG 18 through 21 inclusive, the Aerovane

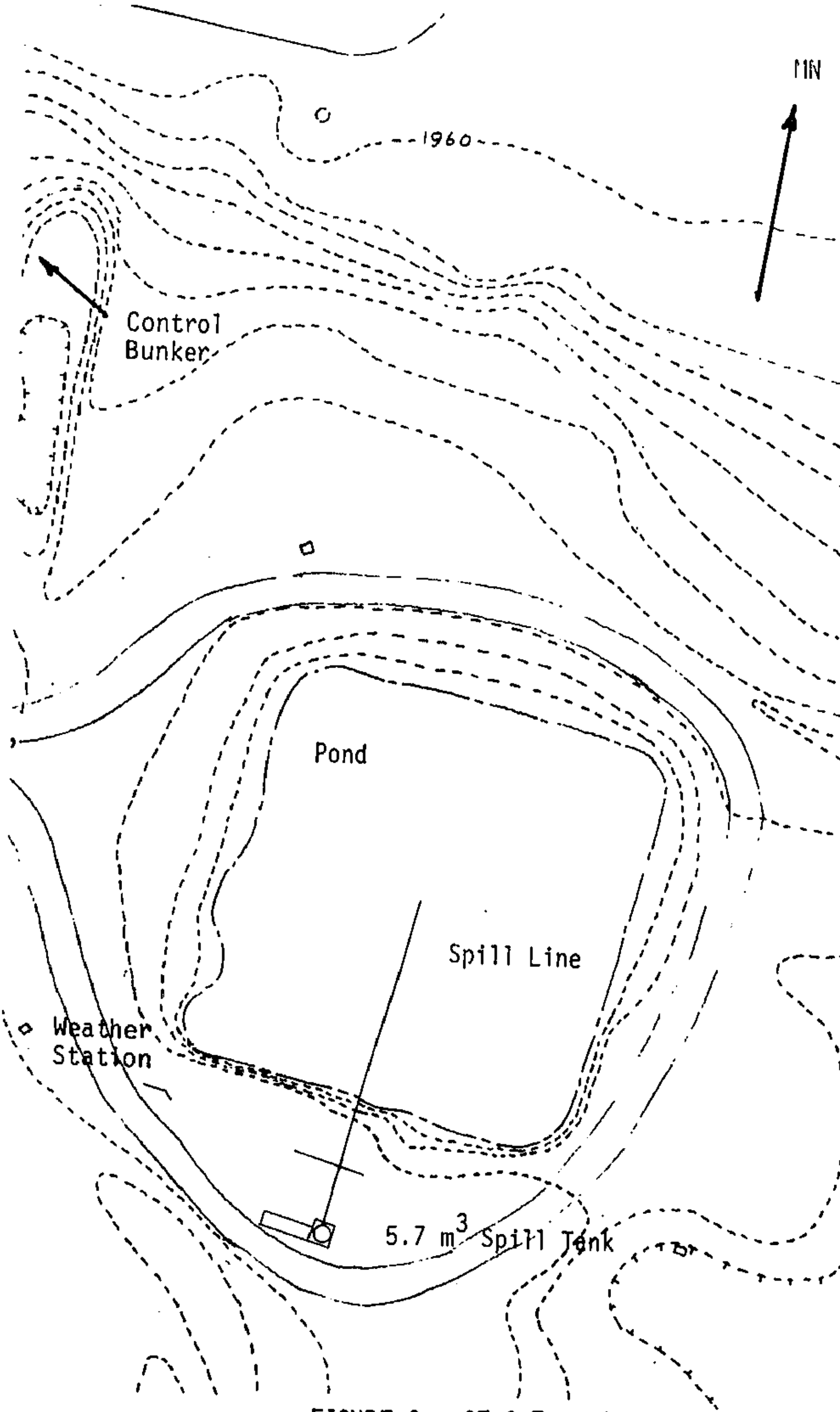

FIGURE 2. CT-6 Test Site

wind sensor was replaced with cup anemometers and wind vanes located at 2 and 10-m elevation. In addition, a temperature sensing element was located at 2-m and differential temperature sensors at 1, 5, 10, and 15-m. The anemometers have a threshold of 0.22-m/s, a claimed accuracy of ± 0.07-m/s, and a distance constant of 2.43-m. The wind vanes have a threshold of 0.22-m/s, a claimed accuracy of 2^{o}, and a distance constant of 1.7-m.

PHOTOGRAPHIC INSTRUMENTATION

Photographic coverage for the experiments was provided by camera at three locations. The crosswind location was on top of the contro bunker 220-m from the spill point. The upwind location was 35-m southwest of the spill point. The overhead camera was suspended between two towers 45-m above ground 120-m north of the spill point. The types of cameras used for each test are shown in Table 1. Measurement markers (1-m square panels) were placed in the field of view of each camera to enable measurements to be made from the film.

TABLE 1. Photographic Instrumentation

Camera Location	Camera Type	Test: LNG- 12	13	14	15	16	17	18	19	20	2
Crosswind	16mm, 100 f/s	X	X	X	X	X	X	X		X	X
"	16mm, 24 f/s	X	X	X	X	X	X				
"	16mm, 24 f/s (IR Film)	X	X	X							
"	70mm, 10 f/s	X	X	X		X					
Upwind	16mm, 100 f/s	X	X	X	X	X	X	X		X	X
"	16mm, 24 f/s	X	X	X	X			X		X	X
"	70mm, 10 f/s							X		X	
Overhead	16mm, 100 f/s	X	X	X	X	X	X	X			
"	16mm, 24 f/s									X	X

RADIOMETRIC INSTRUMENTATION

Two types of radiometers were used to measure the thermal radiation from the flames produced in tests LNG 12-17. The wide angle radiometers* had a field of view of 150^{o}; thus they received radiat from the entire flame. The narrow angle radiometers** had a view angle of 7^{o} and were oriented to receive radiation from a selected

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* Hy Cal Engineering Co., Model R-8015-B

** Hy Cal Engineering Co., Model R-8101-B

are shown in Table 2. All radiometers except Number 3 had sappr
windows. Radiometer 3 had a zinc selenide window.

TABLE 2. Radiometer Location and Orientation

Station	Location	Radiometer Number	Radiometer Type	Orientatio
		For LNG 12, 13, 14		
	From Spill Pt.			
1	60m NW	1	Wide Angle	Horizontal c spill pt.
2	45m NW	2	" "	Horizontal c spill pt.
		3	" "	Horizontal c spill pt.
3	30m NW	4	" "	Horizontal c spill pt.
		5	Narrow Angle	Aimed 2m ove spill pt.
		6	" "	Aimed 4.4m c spill pt.
4	44m SW	7	Wide Angle	Horizontal c spill pt.
		For LNG 15, 16, 17		
	From NE corner of pond			
1	75m NW	1	Wide Angle	Horizontal c corner of pc
2	60m NW	2	" "	Horizontal c corner of pc
		3	" "	Horizontal c corner of pc
3	45m NW	4	" "	Horizontal c corner of pc
		5	Narrow Angle	2.75m over N corner of pc
		6	" "	2.75m over a 5.5m NE of c of pond
4	44m SW	7	Wide Angle	Horizontal c spill pt.

CONCENTRATION MONITORING INSTRUMENTATION

The instrument used to detect downwind methane concentration was the same in all tests, the MSA Combustible Gas Detector.*

The instrument is based on a thermister bridge circuit, with one thermister coated with a catalyst which oxidizes combustible gases. The heat evolved by the oxidization unbalances the bridge and the output is related to amount of combustible gas. The instrument has been found to be rugged and reliable; however in the present application (for which it was not designed) it has several disadvantages. It has a slow time response, it does not distinguish between methane and other combustible gases, and, since it is based on oxidization o the combustible gas, it cannot be used above the stoichiometric rati (9.7% for methane).

In addition to the gas detectors, thermocouples were used to measure the temperature of the vapor cloud. If the assumption of adiabatic mixing is made, there is a direct relationship between temperature and composition of the cloud and a measurement of temperature can be used to calculate the composition.

In tests 15, 16, and 17, five gas detectors were used downwind t determine when a combustible mixture had reached the ignition point. They were insufficient in number to map the location and composition of the cloud. In tests 18 through 21, 15 gas detectors and 29 thermocouples were placed in an array downwind. The location of the instrumentation is shown in Figure 3.

OPERATIONAL CONDITIONS

Operational conditions for the tests are given in Tables 3, 4, and 5.

Table 3 lists the quantity of LNG spilled, the spill duration an the rate of spill. The meteorological conditions given in Table 4 were obtained with the instruments discussed in the section of meteo rological instrumentation. The wind speed and direction are average over the spill duration. The actual records show considerable variation during the period. The LNG analyses shown on Table 5 are of samples taken from the spill tank immediately prior to the tests. They were done by gas chromatography.

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* Mine Safety Appliances Co., Model I-500

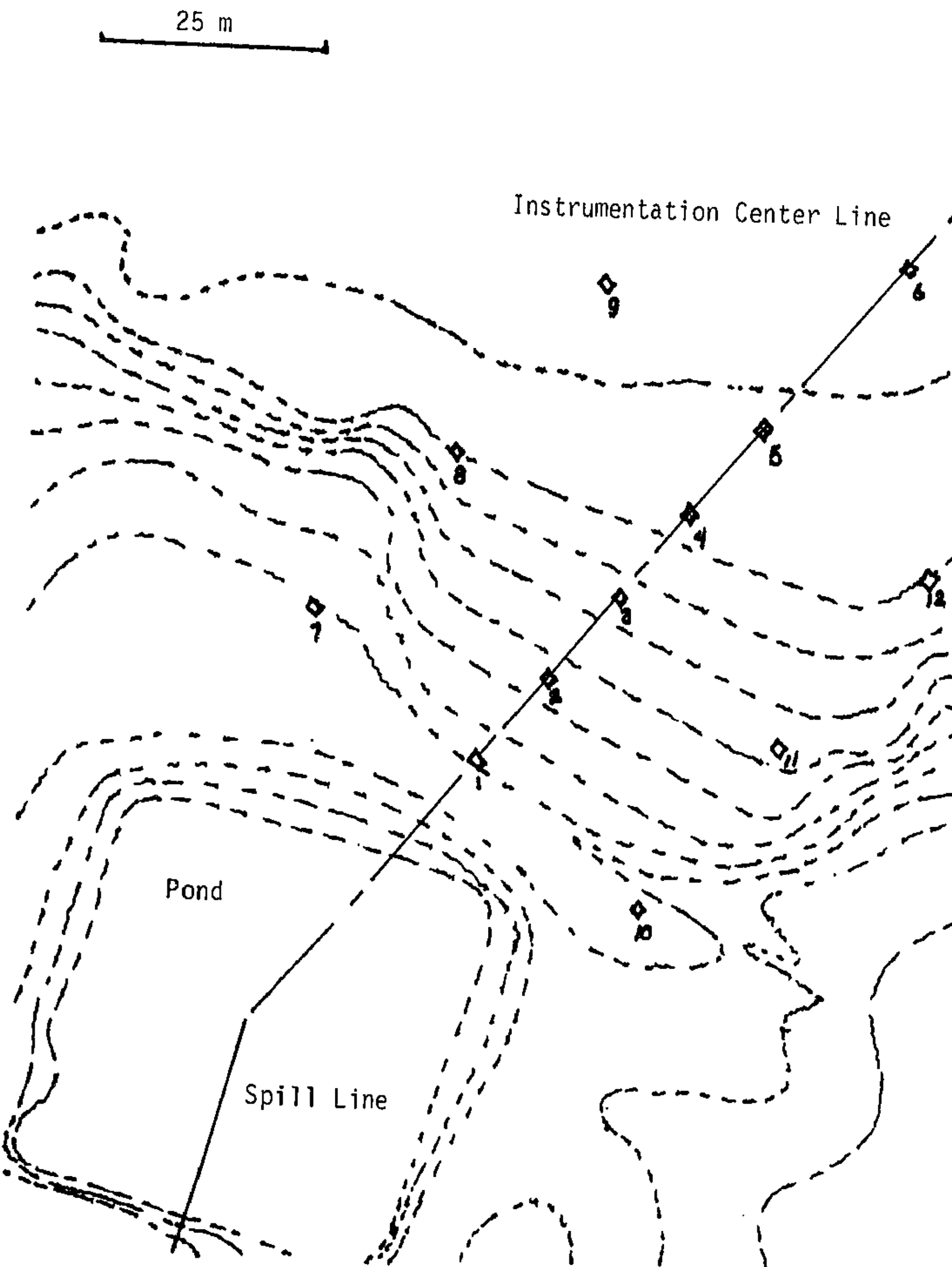


FIGURE 3. Downwind Instrumentation

TABLE 3. Test Conditions

Test	Date	Time	Type	Qty m^3	Spill Duration sec	Spill Rate m^3/min
12	25 May 78	1150	Pool Fire	5.4	81	4.0
13	26 May 78	1019	Delayed Pool Fire	5.7	98	3.5
14	1 Jun 78	0923	" " "	5.5	84	3.9
15	8 Jun 78	2013	Vapor Fire	5.0	75	4.0
16	12 Jun 78	2114	" "	4.4	70	3.8
17	13 Jun 78	1332	" "	5.5	78	4.2
18	31 Aug 78	1456	Dispersion	4.4	67	3.9
19	13 Sep 78	1937	"	4.5	59	4.6
20	9 Nov 78	1526	"	4.5	77	3.5
21	20 Nov 78	1511	"	4.2	53	4.7

TABLE 4. Meteorological Conditions

Test	Temp ^{0}C	Relative Humidity %	Atmospheric Pressure bars	Wind Velocity m/s	Direction ^{0}Mag
12	22	27	0.943	0	--
13	21	36	0.945	2.1	120
14	27	34	0.939	0	--
15	--	--	--	--	--
16	29	33	0.946	7.2	230
17	36	24	0.946	7.2	210
18	36	16	0.939	6.2	205
19	27	29	0.939	5.1	234
20	27	15	0.932	11.3	241
21	20	21	0.943	4.6	200

TABLE 5. LNG Analysis

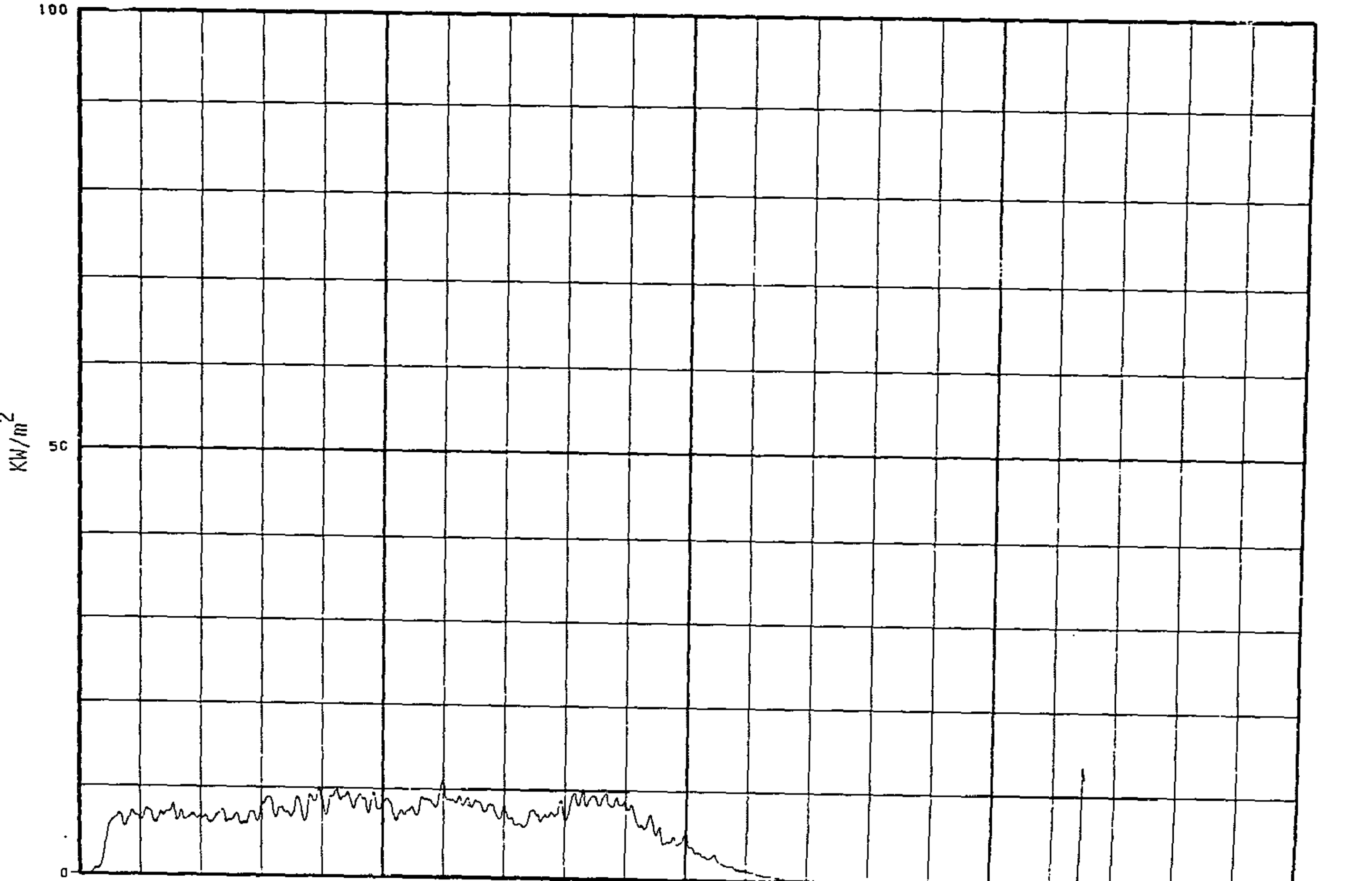
Test	Composition (%) Methane	Ethane	Propane	Higher Hydrocarbons
12	88.04	9.65	2.06	0.25
13	79.19	13.11	4.27	2.10
14	94.87	3.77	1.18	0.19
15	--	--	--	--
16	95.64	3.43	0.71	0.22
17	94.09	5.10	0.71	0.09
18	94.23	4.36	1.10	0.31
19	95.04	3.91	0.75	0.30
20	91.41	8.12	0.33	0.14
21	92.74	4.49	2.31	0.46

RESULTS

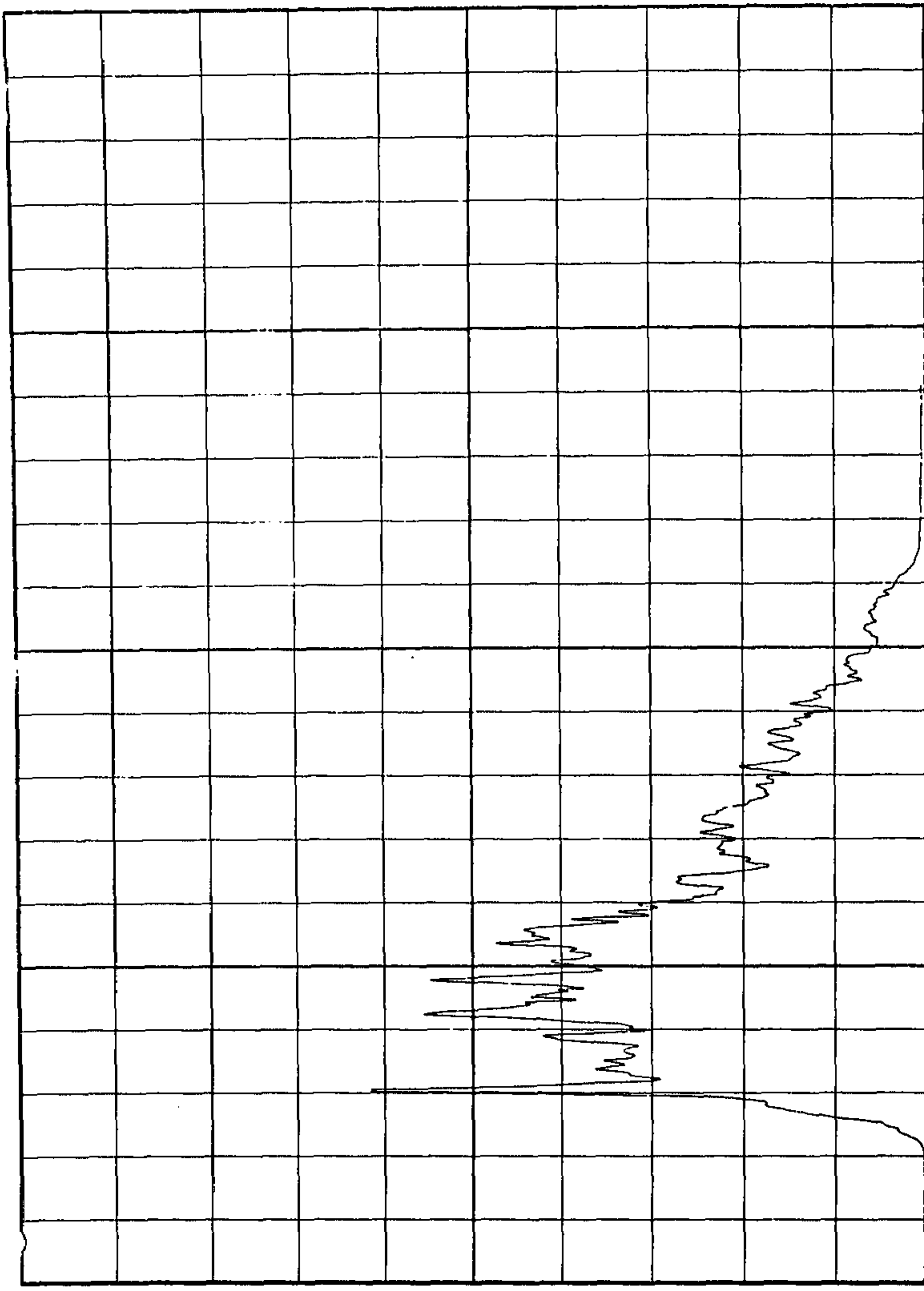
The spill experiments yielded a prodigious amount of raw data. There are 49 rolls of film, 35 radiometer records, 38 meteorological records, 95 gas sensor records, and 116 thermocouple records. Data reduction and analysis is in progress and only a general description and examples of the results will be given.

Test LNG-12 was an immediate-ignition pool fire. It was conducted under calm wind conditions and the flame was a maximum of 8-m diameter and 60-m high. Thermal radiation was measured with seven radiometers. An example of a radiometer record is given in Figure 4.

Test LNG-13 was a delayed-ignition pool fire. A ring of six flares around the spill point were ignited simultaneously 20 seconds after the start of the spill. The delay was intended to permit the LNG pool to reach maximum diameter. There was a slight breeze from the south southeast. This breeze, together with the expanding vapor cloud, covered most of the flares with a mixture too rich to ignite. As a consequence the cloud ignited from only two flares on the southeast side. The cloud burned from the point of ignition, slowly burning the vapor. Throughout most of the spill the vapor production rate was sufficient to prevent the flame from spreading over the entire LNG pool. During the last fourth of the spill, however, the flame did spread over the pool, producing a 15-m diameter, 60-m high flame. An example of a radiometer record for this test is shown in Figure 5.



100
50
0
KW/m²



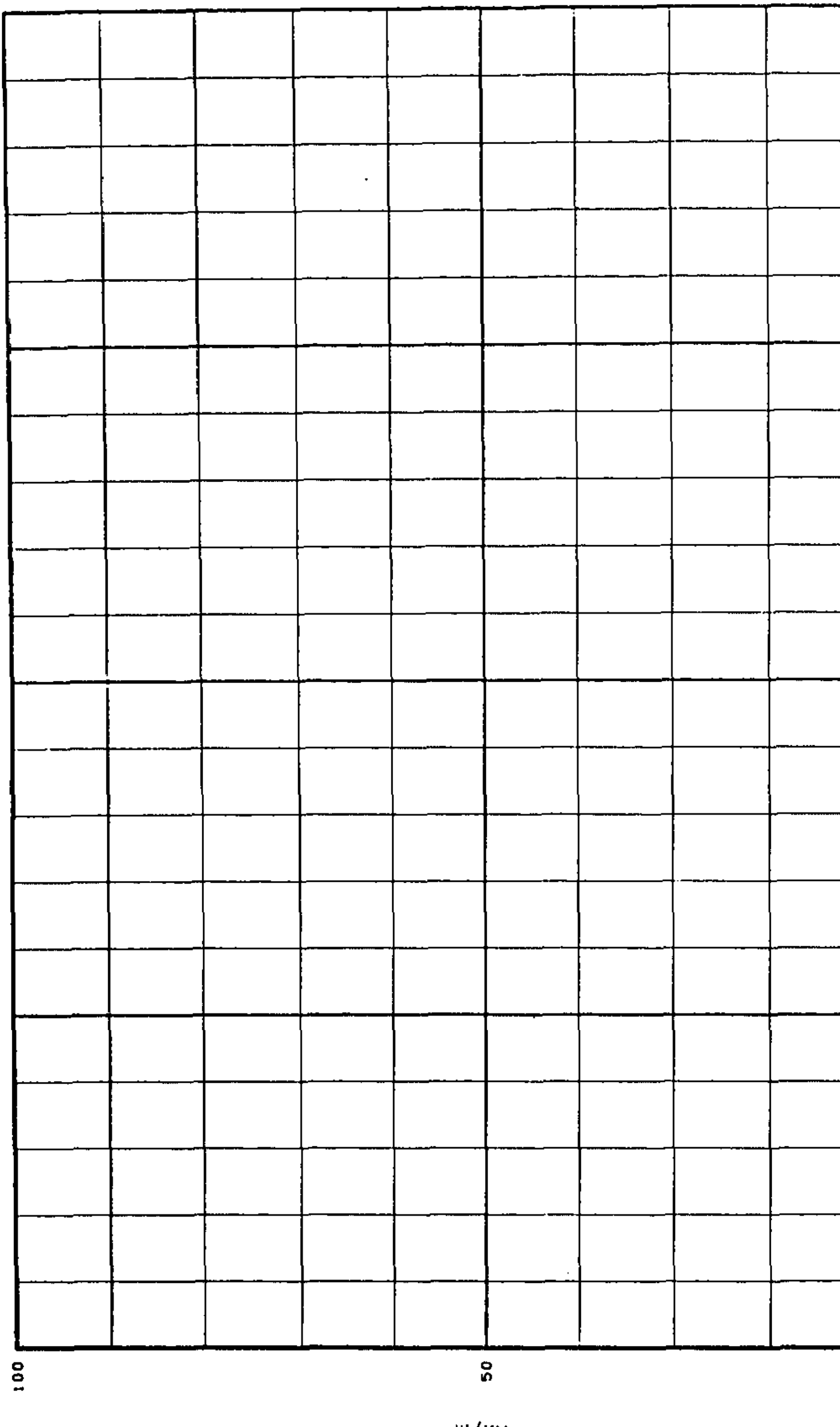
Test LNG-14 was similar to LNG-13. Evidently the vapor production rate and the convective draft caused by the flame were sufficiently rapid in this type of test to overcome the diffusion flame speed, so that the flame is stationary or moves very slowly into the vapor cloud. The flame is thus in the shape of a ring around the LNG pool. This condition lasts until the vapor production rate slows at the end of the spill and the flame is able to spread over the pool.

Test LNG-15 was intended as a vapor burn with downwind ignition of the vapor. At the start of the spill, however the wind shifted from southwest to west southwest and carried the vapor to the east of the flares; ignition did not occur.

Test LNG-16 was a vapor burn with downwind ignition. The test was carried out at night to permit observation of any premixed flame (which is light blue and not visible in daylight). For approximately 10 seconds after ignition this premixed flame was observed as about 10% of the orange diffusion flame. The premixed flame moved faster than the diffusion flame and in about 10 seconds consumed the premixed portion of the front of the cloud and disappeared. Evidently in this type of test only a small fraction of the cloud is in the combustible concentration range (5-15%) and the cloud mainly burns by diffusion of air into the cloud. An example of a radiometer record for this test is shown in Figure 6.

Test LNG-17 was a vapor burn similar to LNG-16, except that it was done in the daytime. The upwind camera showed a good view of a white material remaining on the pond after the spill was completed. This white material looked like ice, but it must have contained trapped gas because it burned with a smoky flame.

Tests LNG-18 to 21 were a series of tests intended to study the downwind dispersion of the vapor cloud without ignition. An array of concentration sensors and thermocouples were placed downwind to determine gas concentration and temperature. All tests except LNG-19 were similar except for atmospheric conditions. Test LNG-19 was done at night to evaluate an instrument that was adversely affected by daylight. Table 4 gives the meteorological conditions for the test. It can be seen that in none of the tests was the wind exactly from the southwest, so the cloud was never centered over the instruments. However, in all tests, concentration and temperature records were obtained from many of the instruments. The extent of the visible cloud for the three daytime tests is shown in Figure 7. An example of a gas concentration record is shown in Figure 8.


100
50
KW/m^2

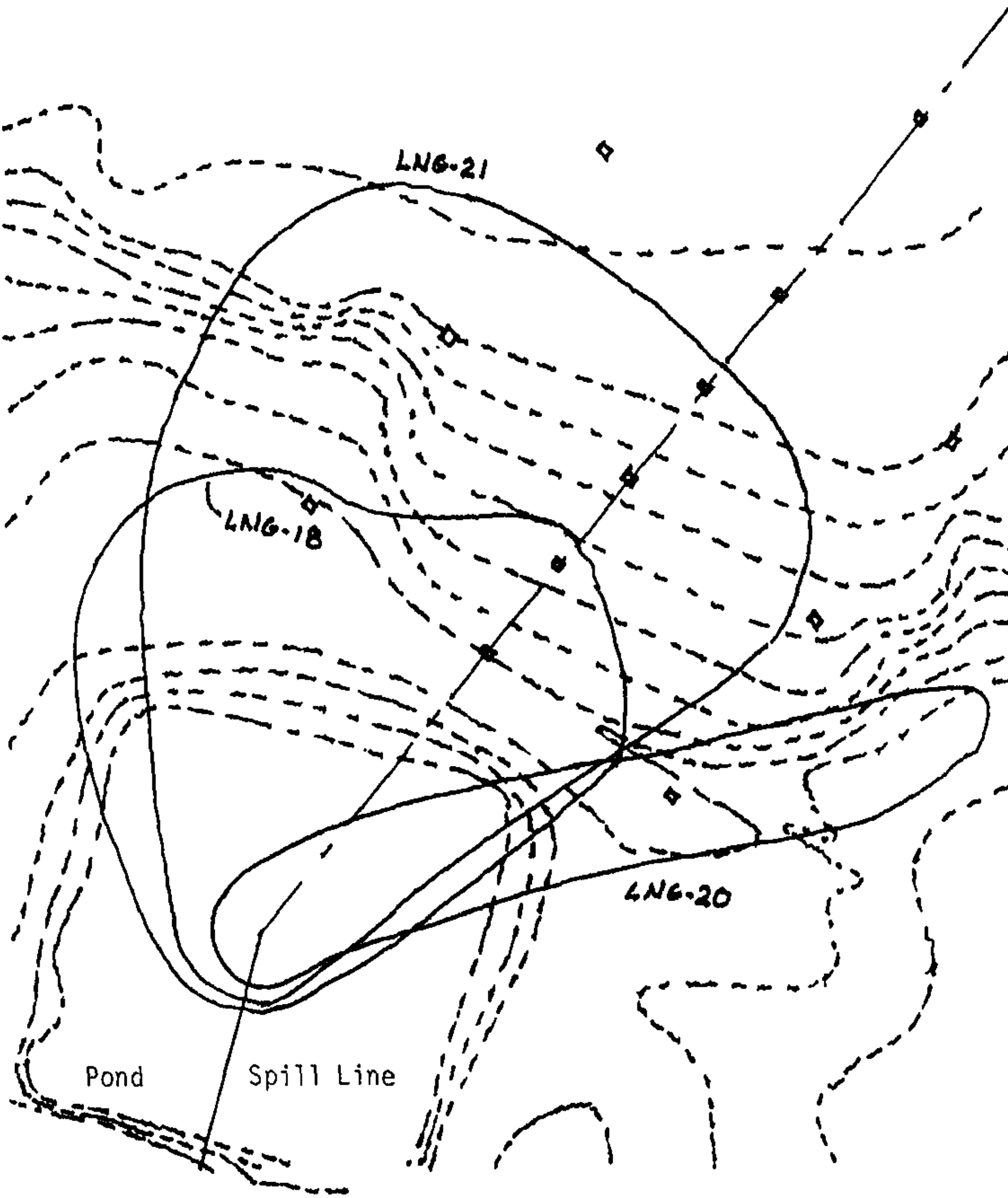
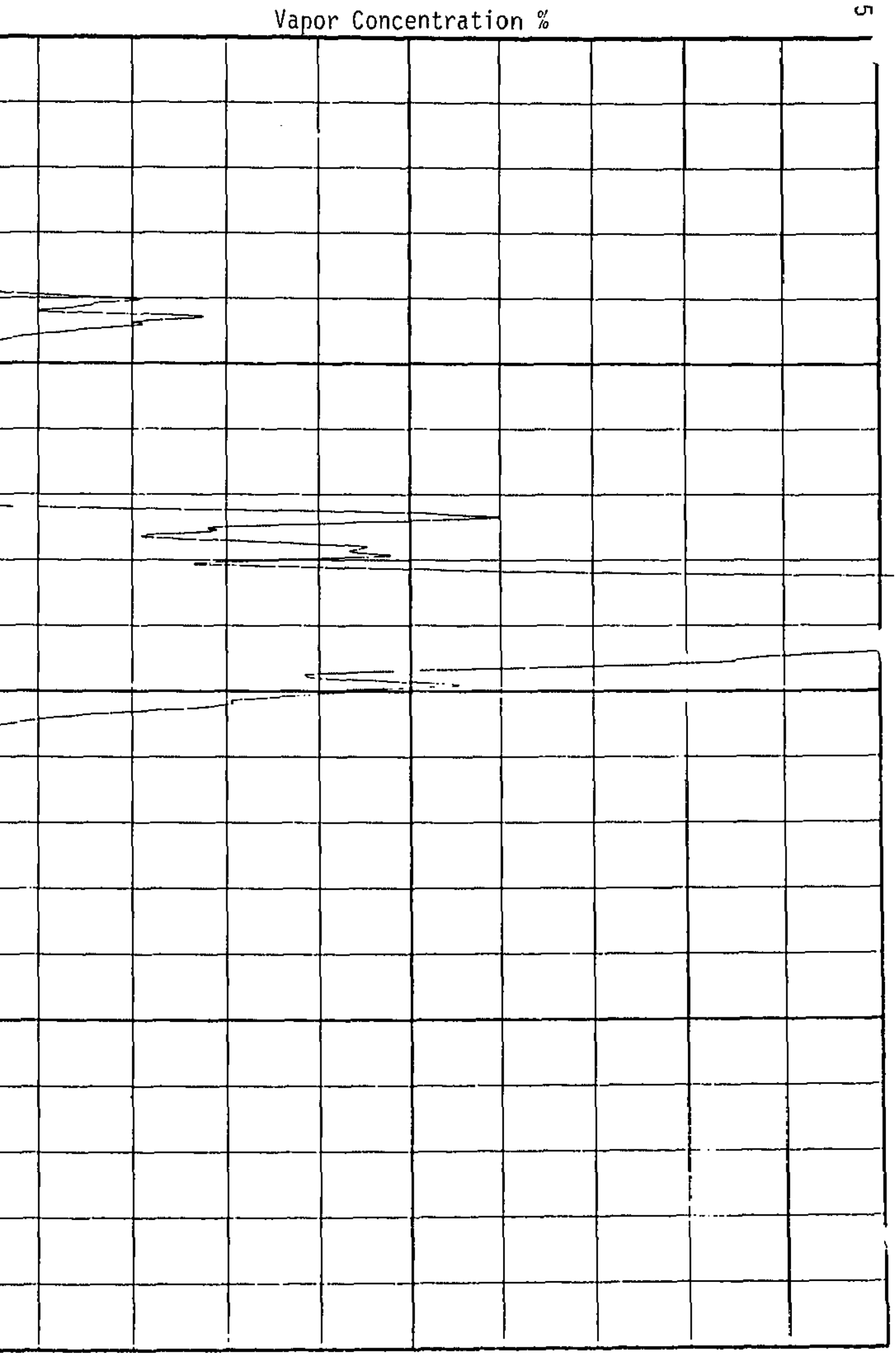


FIGURE 7. Extent of Visible Cloud


Vapor Concentration %
5

REFERENCES

1. C. D. Lind and J. C. Whitson, Explosion Hazards Associated with Spi Large Quantities of Hazardous Materials, Phase I. (U.S. Coast Guard Report CG-D-30-75.), October 1974, ADA001242.

2. C. D. Lind and J. C. Whitson, Explosion Hazards Associated with Spi Large Quantities of Hazardous Materials, Phase II. U.S. Coast Guar Report CG-D-85-77.), November 1977, ADA047585.

REPORT M

Evaluation of Sites for LNG Spill Tests

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se of the study.

CONTENTS

The Department of Energy has been seeking a suitable experimental to investigate the hazards and destructive potential of large spills o liquefied natural gas (LNG). This report describes the evaluation by Lawrence Livermore Laboratory of a number of potential sites that had identified in a previous survey. A list of ten desirable site charact was developed, with the characteristics ordered according to their rel priorities. This list was used in evaluating the potential sites. It concluded that the Frenchman Flat area of the Nevada Test Site is the suitable experimental site for the LNG spill investigation.

EVALUATION OF SITES FOR LNG SPILL TESTS

I. INTRODUCTION

This report describes the evaluation by .wrence Livermore Laboratory of a number of ssible experimental sites to find the one most ıtable for studying the hazards and destructive tential of liquefied natural gas (LNG) spills as ge as 1000 cubic meters. The importation by ship large quantities of LNG poses the threat of large lls. To determine the potential hazards of such lls, the Department of Energy (DOE) is concting a safety research effort that includes comter modeling of the effects of hypothetical LNG lls as well as experimental studies of actual LNG lls to verify the models. The DOE needs a site for ield test facility at which investigations can be de into the potential dangers of spills of LNG d other liquefied energy fuels.

Lawrence Livermore Laboratory (LLL) has en requested by DOE to participate in both the oretical and experimental aspects of the research. are to develop and verify an ensemble of alytical models capable of describing the enomena that can occur in releases of LNG to the vironment. Included will be studies of vapor neration and dispersion, fire and radiation ards, flame propagation and detonation, and ling of the effects observed to the much larger ls that would be possible in accidents.

An extensive experimental program will be reired to verify the analytical models, with tests in.ving the spilling of perhaps as much as 1000 m^3 LNG on water and on land. The experimental nditions will be chosen to explore as wide a varian in the parameters of interest as is necessary to fully test the capabilities of the models. Man spills of smaller sizes (10 to 100 m^3) will be u determine parameters for empirical relationshi develop scaling relationships, or to compile of data for use in the models. Large-scale test be used to verify the models and to provide da extrapolation to accident situations. Some 50 t tests may be required in all.

There is no existing facility at which LNC experiments of up to 1000 m^3 can be carrie reliably and safely. This amount of LNG cor as much chemical energy as 6 kt (6000 tons) o explosives. Although we suspect that the a destructive potential of 1000 m^3 of LNG woul good deal less than that produced by 6 kt of H are unable at present to make a precise evalu of the risks involved because a large numb phemonemological uncertainties exist in rega the behavior of LNG (which, of course, i reason for doing the safety research in the place). We must, however, be prepared for the in our planning for the experiments, since w make every reasonable attempt to investigate w case situations. Continued attention to the saf doing the research program must be an integra of the program itself.

Because of the uncertainties about the risl volved in doing these LNG experiments necessary to choose a site for the experim facility with the utmost care and thoroughnes the same time, because of the urgency of the D needs we must work expeditiously. The DOE a LLL to evaluate the candidate sites with thes quirements in mind.

The site selection flowchart (Fig. 1) represents the method we have followed for site evaluation and selection. For the most part the individual steps are self-explanatory; however, a few of them need to be discussed in more detail.

For our purposes here we only list the types of spill tests that will be necessary to provide input and verification to the predictive models and to provide actual demonstrations of the effects of large-scale LNG spills. A discussion of the experimental needs appears in the next section.

The site characteristics that relate directly to the experimental plan all fall into the categories of

topography and weather
available water supply. All
are considered nonexper
perimental characteristics
they do have a direct impac
schedule.

If every desirable c
perimental and nonexperin
separately, the list would be
ficult to keep in perspectiv
tifying as many of the indiv
we grouped them into bro
Each of these categories wa

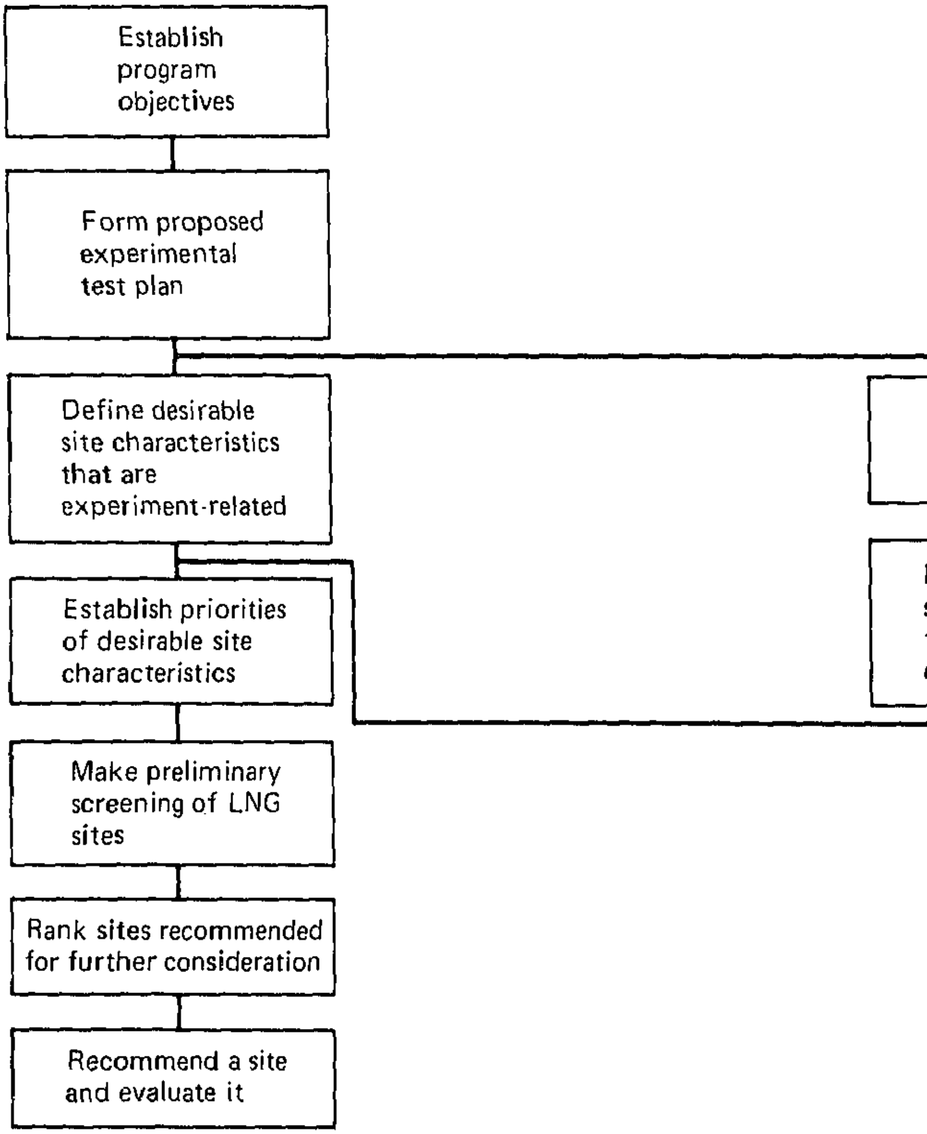


FIG. 1. Flowchart of the site evaluation process used to select an experimental site for large-sca

probably is no perfect site. In fact, even defin- used as the basis for judging the potential

III. EXPERIMENTAL REQUIREMENTS

The experimental requirements outlined here ld not be confused with the detailed experimen- lan for the program, which will be developed Here we only outline the experiment types in r to list topographic and meteorological condi- that are necessary. Once experiment types are ified they can be used as the basis for doing minary safety calculations to determine the ap- riate exclusion area.

The experimental program is expected to con- of some 50 to 100 individual LNG spill tests ng in size from 10 m^3 to 1000 m^3. The first step be to carry out a baseline series of tests. The collected will form the basis of verification for predictive modeling and will act as a cor- one on which all the other tests are based. It is ipated that the baseline series will consist of 20 dispersion tests. They will be conducted under reproducible conditions which are the easiest odel. Ignition will not be attempted. In general, dispersion surface will be used throughout the ine series. Variables will include wind speed, ability conditions, inversion conditions, and surface (i.e., water or land).

After establishing the baseline data, various parameters will be examined to determine effect on the predicted dispersion distances. tests can be conducted in almost any order, ing us to take maximum advantage of the iling weather conditions and thereby minimize duration of the program. Within each series will be spills of various sizes from 10 m^3 to m^3. Smaller spills will be conducted first for new condition.

Effects to be studied after the baseline series in- :

- Gravity effects on sloped land.
- Spill rate.
- Effects of structures.
- Variable topographic relief.
- Rainfall effects.
- Simulated marine conditions.

To evaluate these individual effects on sion, three to eight spills of various sizes are p for each effect. As the LNG program develo the effects of the individual variables becom clearly understood, the number of tests n crease or decrease depending upon the impo of the individual factor being investigated.

First, enough data will be gathered on sion to give us reasonable confidence in the r capability to predict the dispersion distance lower flammability limit (where the cloud and what it will look like) under a variety cumstances. Then various burn tests will be out to determine burn rates and external effe function of ignition time and strength. Fi series of tests will be performed to determine clouds will detonate under conditions a imating those in realistic accidents.

The experimental factors fall into three groups. The first group, and the hardest to c are *those effects which are directly related weather*. These include the wind, temperature sions, atmospheric stability, humidity, an The second group comprises effects related *topography*, including land slope, high reli dispersion surface. Last, and probably most obtained, are those variables which can be cla as *man-controlled*. These include the spill s spill rate, and structures.

IV. DESIRABLE SITE CHARACTERISTICS

The desirable site characteristics fall into two r categories which we have identified as riment-related characteristics (i.e., related to the experimental objectives of the progra other characteristics. The first category i weather and topography. The second categ

cludes all the site factors that are not directly related to the experimental objectives; logistics, safety, administration, and cost are examples which fall into this category.

Experiment-Related Characteristics

Weather

The ideal site should have weather that is sufficiently diverse to permit implementation of the experimental plan within a reasonable time frame and to permit model correlation over a broad range of weather types. Ideally, the seasonal weather should be predictable so that each series can be planned for the appropriate time of year. The test plan should be flexible enough to accommodate the occurrence of desired but infrequent weather conditions. However, knowing that certain weather conditions are more likely to occur at certain times would allow for more economical planning and scheduling of the program.

While it is important for the weather to be changeable it would be best if the cycle of weather changes occurred over a period of days so that individual tests could be scheduled and accomplished with some degree of certainty. The reliability of weather predictions for an area is an important factor. It is also very important that the weather remain constant during the actual time of testing which may be for a period of several hours. Good climatological data should be available for the previous few years.

Winds

It is desirable that the winds should vary significantly throughout the year both in speed and direction. At the actual test location it would be highly desirable if there were a sector toward which the wind seldom blows. Such a sector would be ideal for the siting of the spill tanks and control center. This question, however, is something that would have to be investigated for each site and incorporated into the facility design. Ideally, wind speeds should have a frequency of occurrence as indicated in Table 1.

TABLE 1. Ideal distribution of wind speeds for an experimental site to study the hazards of LNG spills.

Wind speed (m/s)	0	0-2	2-5	5-10	Over 10

Winds that are steady in b
tion are preferred to strongly g
make model correlations more
tant to be able to predict with
the speed and direction of the v
ing the testing period at least
vance of a test.

Atmospheric Stability

Atmospheric stability can
ing the Pasquill-Gifford stabi
most commonly occurring are
E, the ones in which the majori
formed. However, the extreme
cur occasionally so that they
into the experimental program

Temperature Inversion

Both low-level (0 to 300
and high-level inversions (mo
the surface) may be significa
cloud dispersion. Of these
perature inversion the low-lev
the most important at this tim
vertical dispersion and create
flammable cloud to travel
tances—an important conside
vestigated in this series of t
perature inversions may be a
long-range cloud transport; h
effect has not yet been det
perature inversions, particul
perature inversions, occur at
this may be an important cons
a site for night or very early

Rainfall

Rainfall may have a signi
the mixing of the vapor cloud
heating rate of the cloud. The
tion would be to have a site at
seasonal and therefore more p
the rain would fall steadily
tently. The actual rate of rain
significant factor for this prog
effect of a higher or lower rate
ter the test and after the actu
has been determined. It is d
conduct the tests under diff

verse Weather Conditions

Other weather conditions can also be impor-t in that they might preclude conduction of the ts as scheduled or at a reasonable time, or in that y might be so extreme as to introduce unknown ects that would be hard to reproduce. Fog, for ex-ple, if it occurred very frequently, could make it ficult to safely conduct the program. Therefore a that is relatively fog-free is desirable. High midity (>40% relative humidity) will probably ve some effect, while temperature may have little ect on spill phenomenology. Extremes in either of se conditions should be investigated if they oc-.

be of Topography

The slope of the test area both directly upwind downwind of the spill area is important because he effect of gravity on the LNG vapor cloud, ch is denser than air when at low temperature. ally, the site should have a large flat area with a tle slope to one side. This is typical of the large -lake areas found in many regions of the western . By judicious selection of the spill site and wind ctions, many of the planned spill experiments ld be conducted under this condition. For eline testing the slope should be less than 3% and uld extend for 5 km downwind of the spill point. later tests it would be desirable to have a slope bout 5% or so. Finally, tests might be desirable more rugged topography to assess the effect of relief on dispersion. It would be difficult to all three conditions at the same site.

rine Conditions

One of the series of tests to be conducted dur-the experiment is dispersion of the vapor cloud r water. For the larger spills this requires a body vater of considerable size (~ 5 km in diameter). s could either be a naturally occurring body of er on the site, or, if conditions warrant, it could specially constructed. Again, many of the dry areas of western U.S. have water in them dur-rainy seasons and thus would be ideal as sites for ducting spills over both flat land areas and water is depending on the time of the year.

ilable Water Supply

There is one other desirable experimental site racteristic which does not fall into either the ther or the topography classification. That is an supply might be utilized for the constructio much larger lake for the simulated marine tions described above.

Other experimental factors, such as sp and spill surface, are man-made and theref not strongly influence the site selection proc

Other Characteristics

There are considerations relating t desirability of a particular site that are not d related to the experiments. They include such as logistics, safety, administration, schedul cost. All have at most an indirect effect on t periments and they are therefore cons separately from the experiment-related c teristics.

General Characteristics

The ideal site would be a remote preferably owned and controlled by the g ment, in which an exclusion area could tablished. Of prime importance would be t istence of an environmental impact statement would permit the LNG tests or which cou easily modified to do so.

Also of major importance would be a fav political climate for conducting this progra secondary importance would be the close pro of an LNG supply, a labor force for constru operation, and maintenance, and normal u such as water, electrical power, and roads. day's standards, this LNG test facility is not a construction project, so for the period requi establish a test facility and operate it, a labor could be imported from distances up to 100 within reasonable costs. In addition, the ide should rank extremely high from a s standpoint and should not be more than one travel from the LLL home base at Liver California. All of these general characteristics the schedule and cost of the program. They a cussed in detail in the following paragrap should be emphasized that these characte although not directly related to the experi will carry as much weight as factors directly r to the experiments, and in some cases more w The prime example of this is safety, which w discussed at length.

associated with these tests it would not be desirable to have a population center located near the boundary even though it was outside of the controlled area.

The possible effects of a detonation of a 1000-m^3 spill have been estimated and are given in detail in Appendix B. This estimate yields a range of 3000 meters (almost 2 miles) for an overpressure limitation of 0.5 psi, which is the pressure threshold for glass breakage.

Until a specific site is selected and analyzed one must assume that a wind could come from any direction, which results in a maximum-size exclusion area. Individual sites, however, are expected to have limitations on the wind sectors available or suitable for testing. When the wind sectors are identified, smaller exclusion boundaries can be established.

In addition to personnel safety and fire hazards, protection of property must be considered. For this reason areas containing power lines, oil and gas fields, and other property of high value in the region of the cloud dispersion should be avoided.

brush and grass is undesirable of the fire hazard. The site located in an area having spars an area that can be cleared c

Security

Security is not conside problem in site selection in vi for controlled access and an e. precautions would be in effec and transfer of the LNG for any test the area downwind c be patrolled for personnel, c

Administrative Characteristics

As mentioned in the gene it would be desirable to use a facility. This would avoid th quisition and should shorten any special permits or varian tions that might be required.

A site where the LNG ex would have minimal conflict the site would be advantaged

V. PRIORITY RANKING OF DESIRABLE SITE CHARACTERISTICS

After careful examination of all of the previously discussed desirable characteristics, we consolidated them into ten separate categories and ranked them as shown below:

1. Safety.
2. Minimal external constraints.
3. Acceptable surface winds.
4. Flat land.
5. Wide range of atmospheric conditions.
6. Large body of water.
7. Available water supply.
8. Low costs.
9. Rainfall.
10. Variable topography.

The final ranking was achieved by compiling the individual rankings of the scientists and engineers associated with the LNG program at LLL. Every individual ranked safety as the single most important factor to be considered for site evaluation. The ranking of the remaining factors varied only slightly depending interpretation of the categor perception of what was m overall success of the progra

1. Safety

This category includes a and property safety. Desirab cern within this category are at least 16 km in diameter, trolled population within an to the exclusion area, (3) a lo plies sparse vegetation, and (highways, power lines, oil a stations, etc., within the exc

2. Minimal External Const

This category includes a tal Impact Statement (EIS) v made applicable to the LNG

uded in this category are a favorable local
tical climate and minimal conflict with any
er activities and functions of the site. Controlled
al and physical access contribute to satisfying
constraint.

Acceptable Surface Winds

This category implies that for a reasonable per-
tage (~60%) of the time there will be winds of
eptable speed and direction. It assumes that the
ed and direction will be variable, persistent, and
dictable enough to safely conduct the tests.
od past weather records are required.

Flat Land

One of the primary requirements for the
eline spill tests is a relatively large flat area for
dispersion surface. This area should be approx-
tely 5 to 10 km in diameter and should have a
e of less than 3% and preferably zero.

Wide Range of Atmospheric Conditions

Atmospheric conditions that are considered to
f high importance include low-level temperature
ersions (≤300 m) and a wide range of at-
spheric stabilities. Predictability and persistence
important also. To make use of the low-level
perature inversions, the ability of a site to ac-
nmodate testing at night or very early morning is
esirable factor.

Large Body of Water

A body of water approximately 5 km in
meter would be desirable. It will be used to
uate the effect of water on vapor cloud disper-
, as might occur in marine conditions. A
onal lake could provide both a large flatland
and a large body of water during the various
ons.

Available Water Supply

This implies an adequate water supply that can
obtained at a reasonable cost. The minimum
amount required would be that necessary to f
maintain the pond for the experiments inv
spills on water. If a larger supply of water
available it could be used if necessary to con
the large body of water (item 6) and/or to sin
local rainfall (item 9).

8. Low Costs

The overall costs of the LNG progra
dependent upon many factors. Existing su
facilities, existing labor forces, short
transport, and short travel for LLL personn
some of the more obvious ones. Without goin
detailed cost studies and estimates, a rough
parison of site values should suffice for the
selection of potential sites. Very expensive sit
most easily identified.

9. Rainfall

Rainfall may be an important weather c
tion but one infrequently required. A locatior
a short but predictable rainy season woul
desirable. Rain conditions can be artificially cr
for the smaller spills. It would be desirable to
rains of some duration for the larger spills r
than intermittent showers.

10. Variable Topography

One of the parameters to be studied ir
LNG program is the effect of gravity on vapo
persion. Gravity effects are more noticeabl
spills on a sloping topography than for spills
flat surface. Some high-relief areas would be
terest for a few of the experiments. Desirable
ing land would be between 5° and 10° and sh
extend for a distance of about 5 km. High relie
difficult factor to define. The desirable conc
would be to have bluffs, steep hills, or al
changes in elevation adjacent to a site with fl
sloping land, with winds occurring to or from
direction only infrequently.

VI. SCREENING OF POTENTIAL SITES

We took as our list of potential sites for the
G experimental facility an initial compilation by
DOE of installations owned by the DOE and the
tary.[1] Sixty-nine installations having areas
ater than 64 km^2 are included. Reference 1 lists

In view of the limited resources availabl
the site evaluation study, we could not justify
ing an extensive examination of each of the 69
listed. We therefore used only information re
available at LLL. Our sources included at

ations, we used negative factors or gross failure neet one of our ten desired site characteristics as basis for the initial screening. The three egories of desirable site characteristics where se deficiencies were most easily identified were ety (No. 1), Minimal External Constraints). 2), and Low Costs (No. 8).

Table 2 shows the results of this cursory examination. It should be noted that if one strong son was found for rejection of a site, we often did examine that site further in relation to the other eria. Therefore there may be other reasons ides those shown in the table for rejecting any ticular site.

Over half of the installations were found unacptable because of safety considerations. For the st part this judgment was based on the size and pe of the facility, the proximity of large popula- n centers, and the existence of major highways acent to or through the test area. Approximately e-fourth of the installations had obvious external nstraints such as conflict with the installation's me mission or lack of controlled visual or ysical access. One-third of the locations were ged to have unduly high operating costs because remoteness, short testing season, or lack of idenable support or facilities.

Many of the desert sites were similar to NTS in ny respects, but were lacking in both support ilities and in detailed weather data. Some of these es had additional complications; for example, the gway Proving Grounds remain contaminated d therefore unsuitable, Yuma Proving Ground closes a large wildlife area, the Salton Sea Naval eapons Range contains a National Wildlife fuge, and the National Reactor Test Site is for rious reasons unable to accommodate the LNG ll tests.

The nine sites remaining after this initial eening were given a cursory evaluation with inmation available from road maps and the atlas. cept for NTS and China Lake, none of the sites re visited for inspection as LNG test sites. Each the nine sites is described briefly below with the ailable information we have at this time. The site found to offer the most advantages, NTS, is scribed in more detail in Sections VII and VIII.

We made an initial attempt to evaluate each of e nine sites on each of the ten desirable site aracteristics. It quickly became evident that we d not have sufficient funds to obtain the necessary formation to complete such an examination of ese sites. Three of the desirable characteristics inlved weather conditions. Weather records for or of such limited scope as to be of dubious va

Evaluation of actual site conditions woul quire an on-site inspection to develop any degree of confidence in the potential of a site. S it was not practical to visit each of these sites fo evaluation, a general description of the site fa on which information was available is prov here. Certainly there is considerable data mis which would have to be obtained in orde provide a comprehensive evaluation. Attempts made to establish contacts at each of these facil These contacts are included in the general des tion.

Hunter Liggett Military Reservation

General: Army reservation in California, i Central California coast range, approxim 150 miles SE of San Francisco. Encompasses a tion of San Antonio Reservoir. Varied topogra

Weather: Typical of California coastal va some marine influence.

Topography: Varied, generally rugged, lin flat land.

Population: Sparse.

Vegetation: Mixed oakwoods, grassland.

Water: Adequate supply. Emcompasses a tion (1 mi by 5 mi) of San Antonio Reservoir.

Logistics: Travel distances from LLL are reasonable.

Other: Vegetation may be excessive and w require clearing. If so, the site may be environ tally sensitive. San Antonio Reservoir is report be used by the public for recreational purpos this is so, controlled access could be a proble

Contact: Mr. Jack Yamauchi.

White Sands Missile Range and Holloman Air Base

General: A huge area in south central Mexico having dimensions approximately 16 64 km. White Sands National Monument, Sar dres Wildlife Refuge, and Fort Bliss Range within the southern third of the range. Highway 70 cuts across the southern corner other major highways are shown within the b ary. The San Andres mountain range run length of the site, leaving flat and desolate la the east side.

Weather: Typical of high (4000 ft) south deserts. Would be expected to vary seasonall

for the sites that survived this initial screening.

	Approximate dimensions (km)	W ur
ALABAMA		
Fort Rucker	24 × 16	
Redstone Arsenal	11 × 8	
ALASKA		
Fort Greely	48 × 32	
Fort Wainwright	48 × 48	
Kodiak Naval Station	8 × 8	
Yukon Command Training Site	112 × 48	
ARIZONA		
Fort Huachuca	32 × 16	
Luke Air Force Range	208 × 40	
Navaho Army Depot	16 × 16	
Wilcox Dry Lake Bombing Range	24 × 16	
Yuma Proving Ground	80 × 32	
ARKANSAS		
Fort Chaffee	32 × 16	
CALIFORNIA		
Camp Pendleton	32 × 16	
Camp Roberts	24 × 16	
Edwards Air Force Base	56 × 24	
El Centro Naval Air Facility	80 × 32	
Fort Irwin	56 × 48	
Hunter Liggett Military Reservation	40 × 24	
China Lake Naval Weapons Center (North Range)	64 × 48	
China Lake Naval Weapons Center (South Range)	48 × 32	
National Parachute Test Range (Salton Sea)	24 × 16	
San Clemente Island	32 × 8	
Sierra Army Depot	32 × 16	
Twentynine Palms Marine Corps Base	64 × 32	
Vandenberg Air Force Base	32 × 16	
COLORADO		
Fort Carson	40 × 16	
FLORIDA		
Eglin Air Force Base	80 × 32	
Tyndall Air Force Base	16 × 5	
GEORGIA		
Fort Benning	32 × 32	
Fort Gordon	32 × 16	
Fort Stewart	48 × 24	
HAWAII		
Kahoolawe Naval Reservation	16 × 8	
Pohakuloa Training Area	24 × 16	
IDAHO		
National Reactor Test Site (DOE)	48 × 40	
Saylor Creek Air Force Range	32 × 24	
INDIANA		

Smoky Hill Air Force Range	16 x 8
KENTUCKY	
Fort Campbell	32 x 16
Fort Knox	32 x 24
LOUISIANA	
Fort Polk	32 x 8
MISSOURI	
Fort Leonard Wood	24 x 24
NEVADA	
Hawthorne Naval Depot	32 x 16
Nellis Air Force Range	120 x 64
Nevada Test Site (DOE)	64 x 48
NEW MEXICO	
Fort Bliss Anti-Aircraft Range	40 x 32
McGregor Range	64 x 32
Sandia Base (DOE)	8 x 8
White Sands Missile Range & Holloman AFB	160 x 64
NEW YORK	
Fort Drum	32 x 32
NORTH CAROLINA	
Camp Lejeune Marine Corps Base	24 x 24
Fort Bragg	32 x 24
OKLAHOMA	
Camp Gruber	16 x 8
Fort Sill	48 x 8
OREGON	
Boardman Naval Bombing Range	24 x 16
SOUTH CAROLINA	
Fort Jackson	24 x 16
Savannah River Plant (DOE)	32 x 32
TEXAS	
Camp Bullis	24 x 16
Fort Hood	32 x 32
UTAH	
Dugway Proving Grounds	72 x 40
Hill Air Force Range	64 x 32
Wendover Air Force Range	64 x 32
VIRGINIA	
Camp Hill	24 x 24
Camp Pickett	24 x 16
Quantico Marine Corps Base	32 x 16
WASHINGTON	
Fort Lewis	48 x 16
Hanford Works (DOE)	56 x 40
Yakima Firing Range	40 x 32
WISCONSIN	
Camp McCoy	24 x 16

Topography: Extensive flat areas to the east of San Andres mountains. Alkali flats and dry lake s abound.

Population: Sparse. Most of the activities are ated in the southern part of the range.

Vegetation: Anticipated to be sparse in the ali flats areas. The higher regions have juniper piñon.

Water: Scattered springs are shown in the her regions. One lake is shown which could vary ize from 160 to 800 acres, could be alkaline.

Logistics: Oil and gas fields located approx- tely 150 miles to the east could be a potential rce of LNG. Population centers are close ugh to service the program.

Other: Range activities and restrictions are un- own at this time.

Contact: None.

Clemente Island

General: Navy gunnery range off California, proximately 40 miles offshore of San Diego and ng Beach. Shoreline fairly rugged. Topography erally rugged. Highly isolated from public. The e is approximately 8 by 32 km.

Weather: Constant, predictable offshore winds be expected. Some fog.

Topography: Rugged. Limited level land.

Population: Government only.

Vegetation: Grassland, coastal sagebrush.

Water: All around.

Logistics: Sea and air only. 40 miles offshore. pport of major or extended operations may be ex- nsive.

Other: Principal attraction is its isolated rine location. There is little control over sea ap- aches.

Contact: Mr. Jan Larson (Naval Air Station, n Diego, Calif.).

in Air Force Base

General: Air Force gunnery, bombing, and ltipurpose installation in Florida on the Gulf ast, approximately 100 miles east of Mobile, abama. Encompasses 30 miles of shoreline of lf and along Choctawhatchee Bay. Generally oded, low lying.

Weather: Mild weather with few extremes. ould be satisfactory for test purposes. Rainfall equate to excessive. Some fog.

Topography: Low lying, gentle, some marshes, nes.

Water: Along Gulf coast and bays. Pl water.

Logistics: Travel distance from LLL g than most other sites.

Other: Recreational use of waterways n difficult to control.

Contact: Mr. B. B. Toole.

Hill Air Force Range

General: Air Force bombing and gu range in Utah, immediately west of Great Salt Encompasses a 10-mile strip of shoreline and cent salt flats and wet lands. Desert, m vegetation. Varied topography.

Weather: Typical of most desert ranges, table for most tests. Rainfall marginally adequ accomplish tests for which precipitation is req Detailed weather data not available.

Topography: Salt flats, wet lands, port Great Salt Lake.

Population: Sparse, large exclusion area

Vegetation: Sparse.

Water: Adjoins Great Salt Lake. Water shallow over much of site.

Logistics: Access from LLL and proxim local supply centers is about average for th under consideration.

Contact: Mr. Arlo H. Stewart.

Wendover Air Force Range

General: In Utah, south of Hill Air Range, and generally similar. Contains num intermittent small lakes.

Weather: Typical of most desert ranges, a table for most tests. Rainfall marginally adequ accomplish tests for which precipation is req Detailed weather data not available.

Topography: Salt flats, intermittent lake

Population: Sparse, large exclusion area

Vegetation: Sparse.

Water: Unknown. Water table rep shallow, site encompasses intermittent lakes.

Logistics: Access from LLL and proxim local supply centers is about average for the under consideration.

Contact: None.

Hanford Works

General: DOE site in south ce Washington, approximately 70 miles ea Yakima. Encompasses 60 miles of Columbia Low desert vegetation, sagebrush. V *topography*

Vegetation: Sparse.

Water: Columbia River traverses site.

Logistics: Travel time from LLL above average not excessive. Information on local logistics not lable.

Other: DOE installation.

Contact: None.

a Lake Naval Weapons Center

General: Naval weapons development center in fornia, on the Mojave Desert, approximately miles NE of Los Angeles. Desert, minimal etation. Varied topography. Includes two sites: a thern and a southern one.

Weather: Typical hot desert climate, windy at es, would permit a reasonable percentage of test s.

Topography: Mixed, with high mountains on th side of sites. Both the north and south sites extensive.

Population: Large (4000) and generally cen-d at existing test facilities. Controlled popula-.

Vegetation: Mostly sparse, heavy brush in e areas.

Water: Water table is very high at certain loca-s, but in general water is rather scarce. Some ex-g wells.

Logistics: For transport of LNG this location elatively good. Site requires a full day's travel n LLL, Livermore, on scheduled commercial ines, but only about 1-1/2 hours on a chartered LLL plane.

Other: The National Atlas shows the Naval lnance Test Station at China Lake is in two ts. The southern site is shown bordering Fort in to the east. The Naval Weapons Center has eived environmental approval for 40-m^3 LNG ls.

Contact: Mr. C. D. Lind.

ada Test Site (NTS)

General: A large DOE test site in Nevada that been used for many years for underground

Weather: Typical desert climate, would pe a reasonable percentage of test days. Excellent extensive weather records are available for this a

Topography: Variable, includes large areas.

Population: Sparse off-site; on-site popul is controlled.

Vegetation: Sparse.

Water: Winter rains occasionally c shallow temporary lakes in flat areas. Only water supply is from wells on site.

Logistics: Very good in terms of establi support functions on site, rapid travel to and LLL, and available surplus equipment on site could reduce costs of conducting the LNG te

Other: NTS is an established test site unde control of DOE and has long been in use by for other test programs.

Contact: Mr. Mahlon E. Gates (at NVO

Results of the Screening

Various considerations pointed to desirability of a desert site: for example, sa minimal environmental impact, remoteness populated areas, presence of temperature i sions, etc. Most of the desert areas investigated similar weather and topographic characteri and it would have been difficult to choose a them on those grounds. However, in comp other desirable characteristics we found that had many advantages, including excellent re on past weather and an established organizati LLL personnel to provide engineering, geolo photographic, electronic, mechanical, warehou and other types of support. These were impo considerations in leading us to favor NTS ove other candidate areas. Our established wo relationship with the various agencies and orga tions at NTS also led us to believe that the LNG program's schedules and goals could be ach earlier at this site than at any of the others. The two sections of this report discuss in detail th vantages and disadvantages of NTS in genera of the five separate areas within NTS that were sidered for the LNG test facility.

Nevada Test Site for many years as a testing und for nuclear explosive development and er activities. Thus it is only natural that NTS uld be given high consideration as a possible site the LNG spill experiments. Because NTS is a ge site devoted to research and development ac-ties involving hazardous experiments, it does e many advantages not found in similar remote ert facilities.

aluation on Basis of Ten Most Desirable e Characteristics

The general characteristics of the Nevada Test e were examined with respect to the ten desirable characteristics given in Section V. The results of s general examination led to the investigation of e different areas at NTS: Frenchman Flat, Yucca t, Jackass Flats (NRDS), Buckboard Mesa, and d Valley. The following discussion covers both overall aspects of the Nevada Test Site and cific advantages and disadvantages of the five ferent areas. Figure 2 shows the location of these as in the Nevada Test Site as well as the general ography of the site.

1. Safety. NTS has been used for many years as test site for nuclear explosive development. The ety record for the execution of these high-energy, entially dangerous experiments has been ex-lent. Accidents and mishaps have been limited to type normally found in the construction in-stry but with a much lower frequency of oc-rence than would be expected in operations of s size. There are numerous reasons for this good ety record, but the primary one is that all in-ved personnel are aware of the serious conse-ences of performing an unsafe act when con-cting experiments of this type. This attitude is ex-cted to prevail at all working levels during the IG spill experiments.

NTS covers an area of approximately 40 by km. It is an arid desert terrain with sparse vegeta-n, and thus the fire danger is minimized. The pulation working on the site is tightly controlled; tain areas are routinely evacuated during test riods. The area surrounding NTS is sparsely pop-ted. Nellis AFB bounds the site on three sides. ghway 95 runs parallel to the south boundary ap-oximately 5 miles outside the boundary. Lathrop ells, a community of 40 people, is located just outside the SW corner of the site. Indian Sp AFB (population <1800) is located about 14 east on Highway 95.

Many areas in NTS satisfy the safety req ments. The safety features of the different area considered vary only slightly. Frenchman (~10 miles inside the southern site boundar removed from the major activities at the however, a shallow burial facility for low-radioactive waste exists a few miles north of the of interest. Buckboard Mesa and Mid Valley ar removed from the test site activities but are remote from fire fighting equipment. There is activity at Jackass Flats with the Radioactive V Disposal Program. Natural wind drainag Jackass Flats flows down Forty Mile Canyon leads directly into Lathrop Wells, which would safety concern for the LNG spill tests.

Frenchman Flat has one other possible s consideration. There are low-level radioactive remaining on the lake bed as a result of past nu tests. This matter is discussed further in tion VIII.

2. Minimal External Constraints. Initial quiries into the use of NTS as a possible LNG test facility have been favorable. It appears tha LNG program could be carried out without u interference with or from the nuclear test progr

Since both the LNG Program and NTS controlled by DOE, a minimum amount of i agency interaction would be required if the L test facility were located at NTS. The only inte tion identified thus far is with Nellis AFB. C coordination is required since some operations planned in which hazardous amounts of I vapor will drift out of NTS and into Nellis and we plan some ignitions and instrumentation w Nellis. However, since atmospheric nuclear have been carried out in this same Nellis area, is ample precedent for this cooperation; and, in the administrative mechanisms for securing cooperation already exist and appropriate inqu have been initiated.

The Environmental Impact Statement fo Nevada Test Site has recently been updated. newly approved EIS,[2] dated September describes in detail the environmental effects o underground nuclear test program, which is principal activity at NTS. Activities other nuclear testing are described in more general t and treated by comparing their impact with th

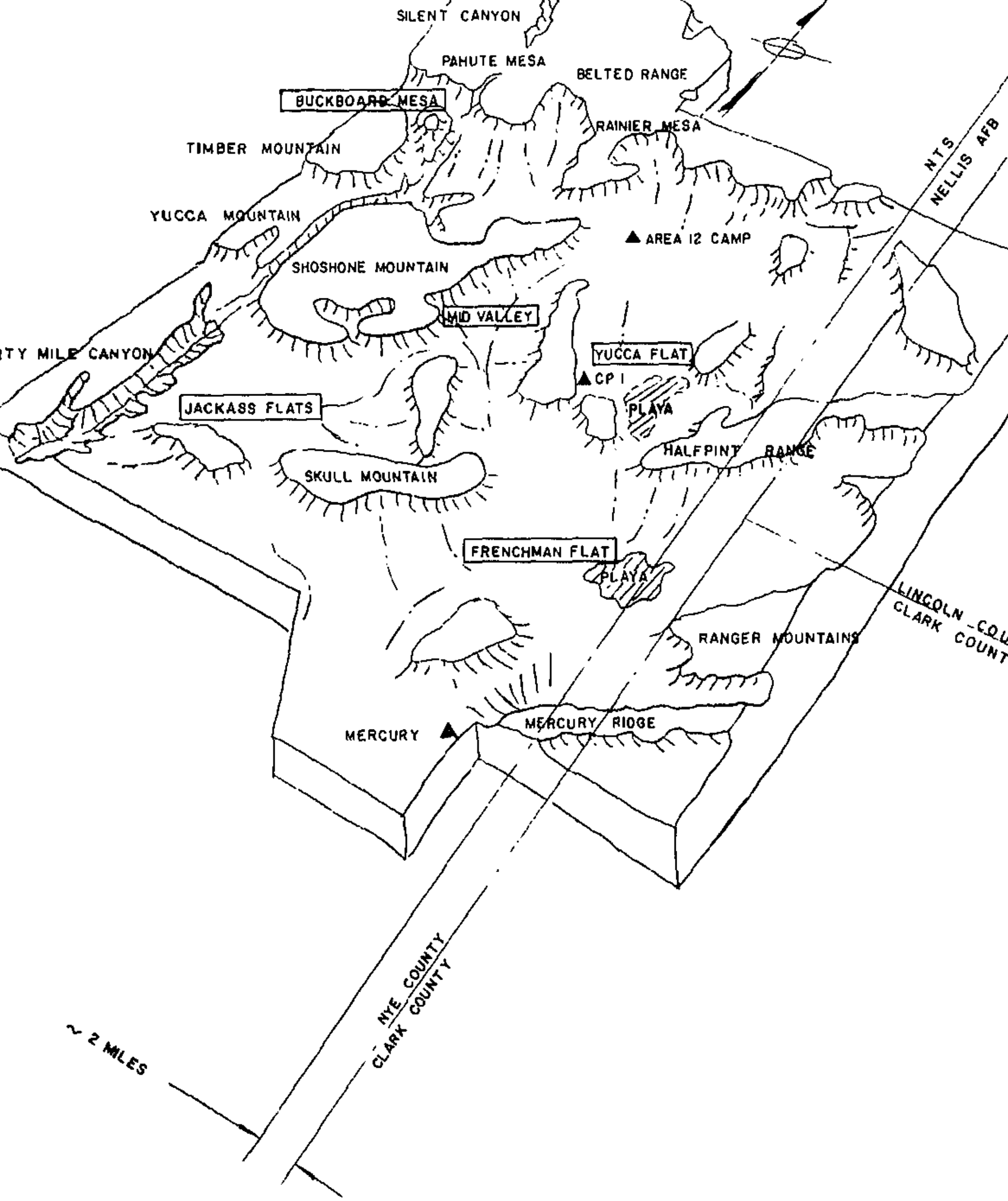


FIG. 2. Topography of the Nevada Test Site (NTS).

clear testing. The section of the EIS covering her activities begins:

"The underground nuclear test program described above constitutes the primary effort at the Nevada Test Site. However, as has been the case in previous years, the experimental program will include a variety of nuclear and nonnuclear projects and experiments wherein

the ERDA laboratories and ERDA co tors, as well as other government agenci their contractors, take advantage facilities available, the climate, the remo and the controlled access of the Nevad Site. Such projects and experimen necessarily conducted on a basis not to fere with the primary mission and

associated with one of the underground nuclear tests, are usually conducted in parts of the test site remote from the areas used for underground nuclear testing. Those which are expected to take place are described here. It is expected that additional experiments similar to these, but not yet identified, will also take place."[2]

One category of experiments described in the S involves the use of chemical explosives:

"This category includes a wide variety of tests employing chemical explosives in one form or another, static or dynamic, inert testing or explosive testing."[2]

In assessing the impact of other NTS activities EIS concludes:

"As regards other activities at the NTS for the most part effects are registered immediately and those effects are very small in comparison with the effects of underground nuclear testing."[3]

The EIS notes that to date 27 square miles of itat has been permanently removed from use by llife and vegetation due to the installation of ds, power lines, support facilities, etc., and that itional plant cover has been disturbed due to road vehicular traffic.

Each underground nuclear test disturbs up to square mile of habitat due to the formation of sidence craters. There have been several hundred lerground tests at NTS to date, and it is anpated that they will continue at about 20 or so year.

The largest LNG experiments ($1000\ m^3$) ld, in the worst case, burn or scorch vegetation r an area of up to 4 square miles.[4] Only a few of se largest tests need be conducted, and they uld probably be done within the same scorched a. The portions of Frenchman Flat that have any etation at all are only sparsely covered, and refore range fires are not likely. In any event, n tests will be carried out with appropriate fighting equipment available. The burning and rching of what little vegetation exists will not troy the root structures. Thus the rate of overy will be relatively fast. It has been estimated t the soot, dust, and unburned hydrocarbons naining after a test will most likely be within the ndards imposed by the Clean Air Act when they ve the NTS/Nellis boundaries.

program. It would appear that the DOE's N Operations Office (NVOO) agrees with this c sion in principle. A letter from that office s

"It appears that the Environmental I Statement for the NTS adequately cove proposed LNG experiments."[5]

A second letter repeats:

"We would expect, based on our discu with LLL staff to date, that the current E suffice."[6]

NVOO is, however, asking that we perfo vironmental impact studies during the progr confirm this belief. Since we will be exter monitoring the phenomena which occur in tests anyway, such environmental studies sho only a small increment over our other effor

Since our larger tests in this area sometimes involve the dispersal and burni natural gas within the portion of Nellis AFI tained in the Frenchman Flat basin, we mus sider whether such activities would be cover the current EIS for Nellis AFB. As mentio another part of this section, NTS and cooperate closely, and for all practical pu Nellis allows NTS to take the initiative in gov activities within the entire basin. The standa ordinating mechanisms have been activated. we were asked by the designated authorit Nellis to write a few-page description of t pected environmental effects,[4] they have inf us they do not expect to have to modify current EIS. Other parts of Nellis are used to tice dropping incendiary weapons, and we anticipate that our impact will not be unlik described for those uses.

3. Acceptable Surface Winds. Excellent w records have been maintained for many ye part of the NTS safety program. Acceptable s wind conditions exist at Frenchman Flat, Flat, and Jackass Flats; less acceptable, st winds are expected at Buckboard Mesa an Valley.

4. Flat Land. Frenchman Flat and Yucc (also called Frenchman Lake and Yucca La their names from the large, flat, dry lake bed lie in shallow basins. Either of these lake beds satisfy the requirements for flat land. Jackass has no dry lake bed and is a gently sloping a plain that is cut along one side by Forty Mil yon. Buckboard Mesa is flat but of very limi tent, while Mid Valley has only gentle to mo

ably be realized at Frenchman Flat, Yucca , and maybe at Jackass Flats.

6. **Large Body of Water.** During the winter and spring months both Frenchman Lake and ca Lake are sometimes flooded. Although the nt of the flooded area is not as large as would be red under ideal conditions, it should suffice for t of the spill tests. The fact that the flooding is onal is an advantageous condition because dision can be conducted over flat land and water n a single facility. Jackass Flats, Buckboard a, and Mid Valley have no body of water.

7. **Available Water Supply.** Other than the onal rains the only available water supply at S is from wells. Frenchman Flat, Yucca Flat, Jackass Flats all have wells in the area which d be used to supply water for a spill pond but ch could not support a large water body needed mulate a marine environment, expecially during summer months. There are no wells in the other areas.

8. **Low Costs.** NTS ranks high in this category several reasons. First is the existence of a sizable port force provided by a government contractor, nolds Electric Company (REECO). This contor provides all types of construction and mainnce personnel to the DOE and the Laboratories zing the site. Other government contractors vide such services as engineering, security, etc. fact that these contractors have been providing with support for many years and are presently lable would avoid many problems entailed in fing a new facility.

LLL has established a convenient, rapid access NTS via daily F-27 flights Monday through Fri- between Livermore, California, and NTS. LLL onnel working on the LNG Program would exence minimum loss of time due to travel.

There is an estimated $1 million worth of sur- equipment at NTS which would be available use there at a fraction of its replacement cost. ne of this equipment, such as LNG storage ks, would require considerable procurement if it had to be fabricated by contractors.

Yucca Flat and Frenchman Flat have lowneability soils coupled with extensive flat areas ch will facilitate pond construction, as opposed he other areas which are either not flat or have ly permeable soil. Pond construction at either hese two sites would be considerably less expen- .

9. **Rainfall.** As with most desert sites, NTS is ed for its low rainfall. Rain can be expected and values much above that are unlikely.

10. **Variable Topography.** Of all the desi site characteristics, topography is the most f All the other characteristics can vary with tin circumstance, but topography changes very sl or at great expense. The desire for sloped an rough land is in conflict with requirement 4 Land), and at any one location it would be dif to obtain both. However, there are several loca at NTS that could provide a variety of topogra conditions if one were willing to relocate the point. This is certainly not an unreasonable proach for the smaller size spills. Both Mid V and Buckboard Mesa offer a variety of condit

Summary of Nevada Test Site. Most o desert sites investigated seemed to share si weather and topographic characteristics, as w be expected. Considering these items alone, would find it difficult to select from among t However, when one compares other desi characteristics, one finds that NTS has many ad tages. In addition to those mentioned earlier in section, there are several others. For example, result of the nuclear testing program, the NTS has assembled over the years a very complete s weather records and has developed a good pr tive capability. Information of this depth is fo most part nonexistent at most remote desert a Another advantage is that LLL has an establ organization of its own personnel at NTS to pro engineering, geological, photographic, electr mechanical, warehousing, and other types of port.

NTS is not without some disadvantages. of these is the low-level residual radioactivity exists in some areas. LLL's long-term associ with this and similar problems leads us to be that this difficulty is one we can easily cope There are several methods for dealing with problem.

A second concern is interference with nuclear weapons test program. To avoid con some areas at NTS cannot be considered. How NTS is a large site, and with only minor sch conflicts it could easily accommodate both tivities. Frenchman Flat is not now used for nu testing.

Comparison of Five Candidate Areas Within NTS

A brief summary of the advantages and d vantages of the five locations investigated at

Frenchman Flat. Closest of the sites (10 miles) ...e main base camp of Mercury, Nevada, ...chman Flat was the location of some of the ... atmospheric tests in which nuclear explosives ... detonated on towers. Many of the test struc... remain on the lake bed, which is dry most of ...year and extremely flat. During the rainy ...n, a large shallow lake often exists for a few ...hs until it disappears by evaporation. There ...oads in the area and several wells nearby. The ...t well is part of a groundwater migration ex...ent by the USGS. The well has been produc...00 gpm continuously for several months. This ... has been diverted to the north end of the lake ...where man-made dikes channel it into a long ...w shape. Electrical power exists in the area. ... are many roads and trails in the area; but ...without them, the surface is so flat that move... from one point to another overland would not ... problem. A very good history of the weather ...endix D) exists for this location since a ...her station has been operating here for 13 ... The winds are variable and predictable. With ...xception of a low-level radioactive storage site ... north end of the basin, there are no major ac...s in the area with which the LNG spill tests ... conflict.

Yucca Flat. Yucca Flat is the next basin north ...renchman Flat. It has the same general ...graphy as Frenchman Flat but is slightly ...er in overall extent. This location would be ...good for the LNG spill experiments except that ... along the southern boundary of the current ...ar testing area. The Test Programs Control ... is situated in the hills just above the SW cor... of the dry lake area. Numerous warehouses, ...y yards, and maintenance shops are located ... the SE boundary of the lake bed. This area is ...within the evacuation boundary during nuclear conflicts with the prime mission of NTS.

Jackass Flats. Jackass Flats is the locat... the Nuclear Reactor Development Site (N... Most of the activities in this area were shut ... several years ago, and very few of the sca... structures in the area are occupied today... specific area investigated is several kilo... southwest of most of these structures. ... topography can best be described as a broad ... sloping valley. It is cut lengthwise by Forty... Canyon, which at this point is a ravine ap...imately 20 meters deep by 200 meters across... soil is composed of sand and gravel with a hig... meability and therefore unsuited for impound... body of water. The town of Lathrop Wel... Highway 95 is 8 miles downslope and gen... downwind during fall and winter. The NTS b...ary is 6 miles from the spill point. This area ha... to recommend it other than existing roads, ex... power lines, predictable winds, and noninterfe... with the nuclear test program.

Buckboard Mesa. This is one of several r... areas at NTS. Topographically it is a small ... bounded by canyons on three sides. The amo... flat land is limited and covered mostly with ... and sagebrush. There are no existing facilitie... as power lines, wells, paved roads, etc. W... history at this location has not been documen... it has at other NTS locations. This is the ... remote of the sites considered, and considera... pense would be incurred to develop it as an ... spill facility.

Mid Valley. This also is a remote locat... NTS, a valley bounded on two sides by reaso... steep hills. The floor of the valley is a few kilo... wide and has a moderate slope. There is ver... flat land available. Like Buckboard Mesa, thi... undeveloped location without paved roads, p... or water. Little weather history is available.

VIII. DETAILED EVALUATION OF THE FRENCHMAN FLA... AREA OF NTS

All of the available information concerning the ...chman Flat area was evaluated in terms of the ...desirable characteristics given in Section V. ...al on-site visits by LLL program personnel ...made to this location to review its current con... and its suitability as an LNG spill location. ...es 3 and 4 are aerial views of Frenchman Flat. Figure 5 shows the estimated hazard zones f... LNG spill tests. The proposed spill site is ne... bermed water area on the north side of the la... as indicated in Fig. 6.

1. **Safety.** With one exception, the di... site for low-level radioactive waste, there ... ongoing activities taking place in the Fren...

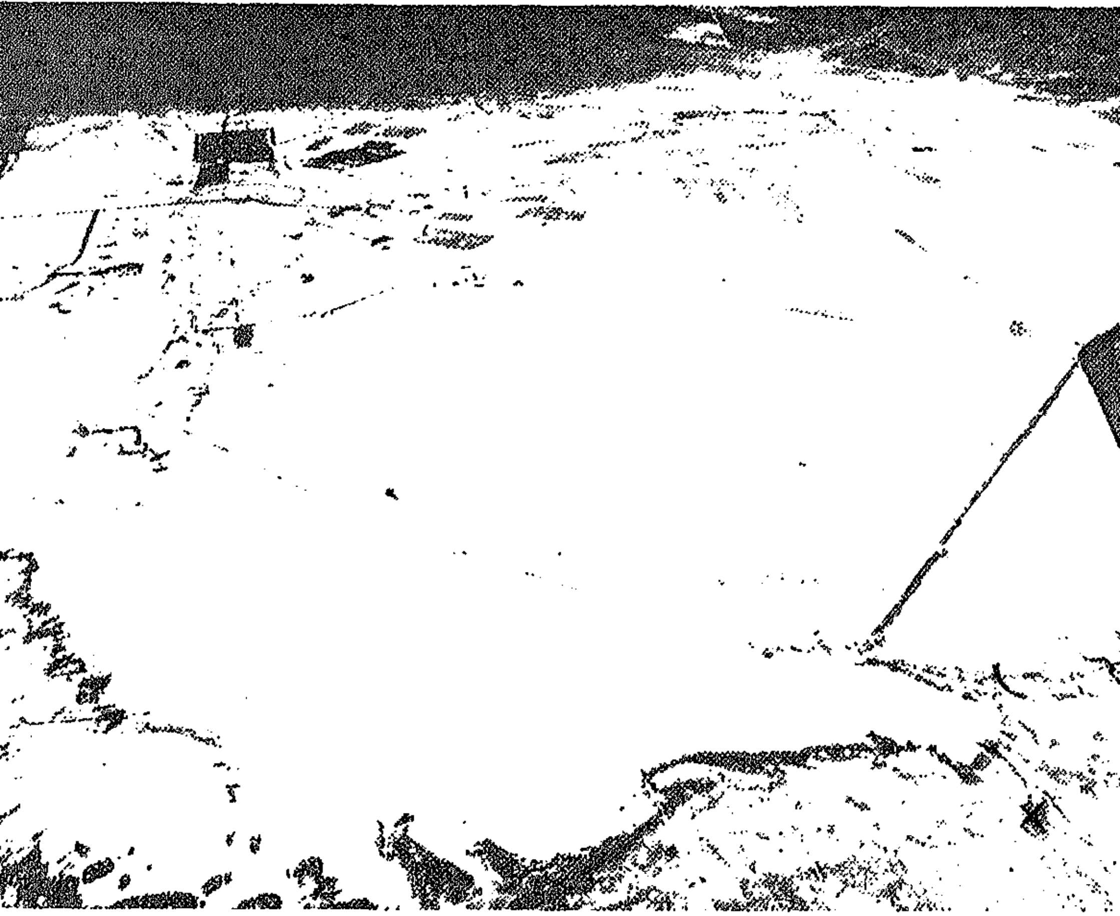


FIG. 4. Aerial view of Frenchman Flat looking south.

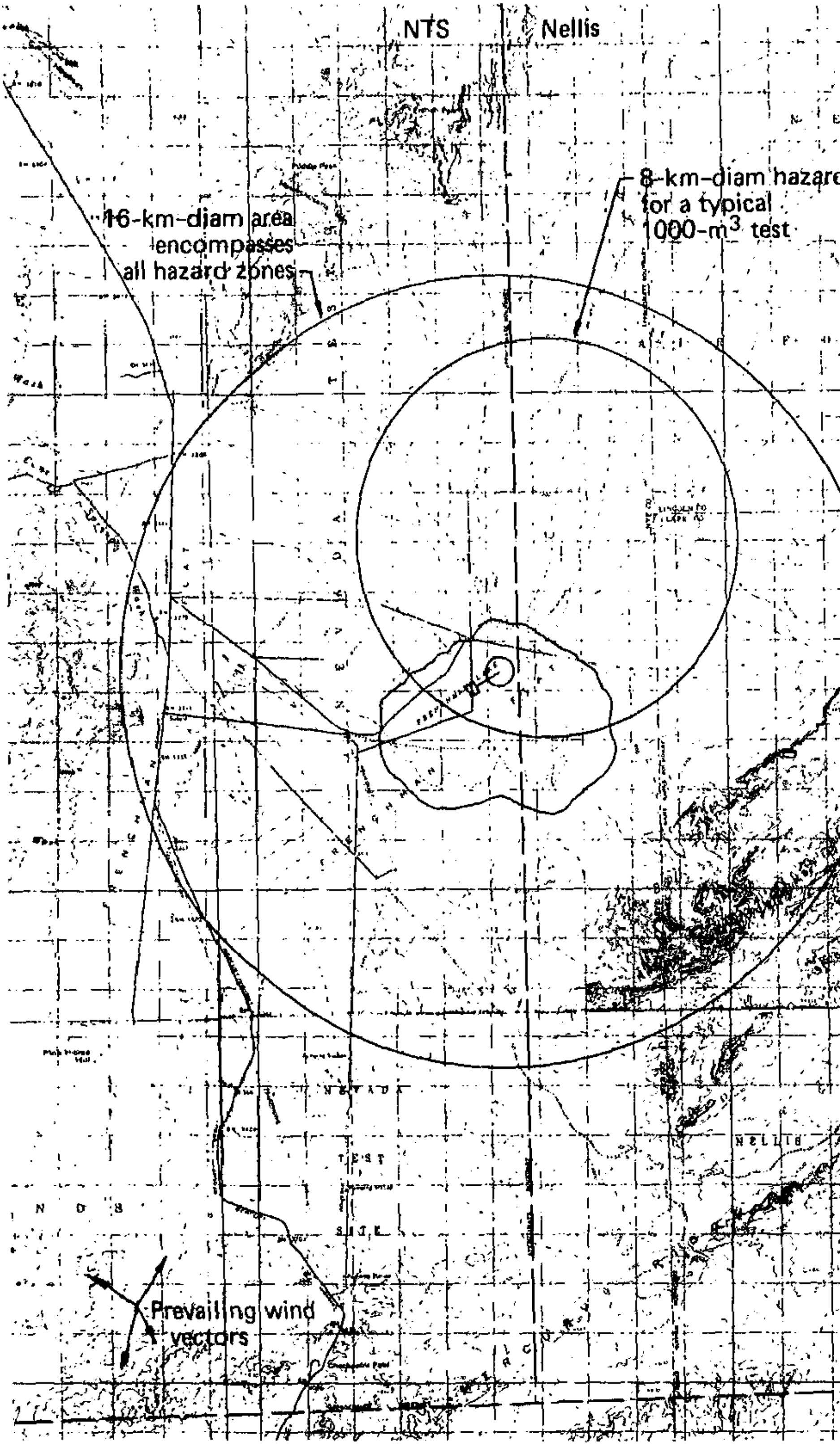
lculations we can conclude that even under st assumptions there would be no radioac- ris hazards generated outside the controlled hould this remain a concern in spite of these ions, there are several reasonable steps that taken to avoid this problem. The existence ual location of the radioactive hot spots can ecked. If they are located, there are several s by which the soil can be economically ed to avoid the creation of dust from either activity or uplift from a detonation. , once these areas are more clearly defined, n be taken to avoid them.

ermal effects resulting from cloud ignition ted in Appendix E. These predictions are luded in the safety zones shown in Fig. 5.

Minimal External Constraints. As discussed ection on safety, there are few activities in nchman Flat area. The site itself is approx- 16 km north of Mercury, the main base f NTS.

planned that dispersion of LNG vapor and burr the clouds will sometimes be carried out on Ne Discussions between NVOO and Nellis perso *concerning this plan have taken place.* NTS/Nellis boundary divides Frenchman basin almost in half. Nellis has no project in its of the basin but NTS has carried out projects in basin which encroached well into the Nellis half cluding atmospheric nuclear tests. According mechanism for close coordination between and Nellis has existed for many years. For all p tical purposes NTS is considered accountable the entire Frenchman Flat basin.

The Environmental Impact Statement, cussed in Sec. VII, will not be discussed further except for one point. Several years ago an dangered plant species of milk-vetch was repo found at a few spots in the south end of Frenchman Flat area. Since that time gravel *have been developed which cover some of the a* indicated. Recently this plant species has



NTS
Nellis
16-km-diam area encompasses all hazard zones
8-km-diam hazard for a typical 1000-m^3 test
NEVADA
TEST
SITE
NELLIS
Prevailing wind vectors

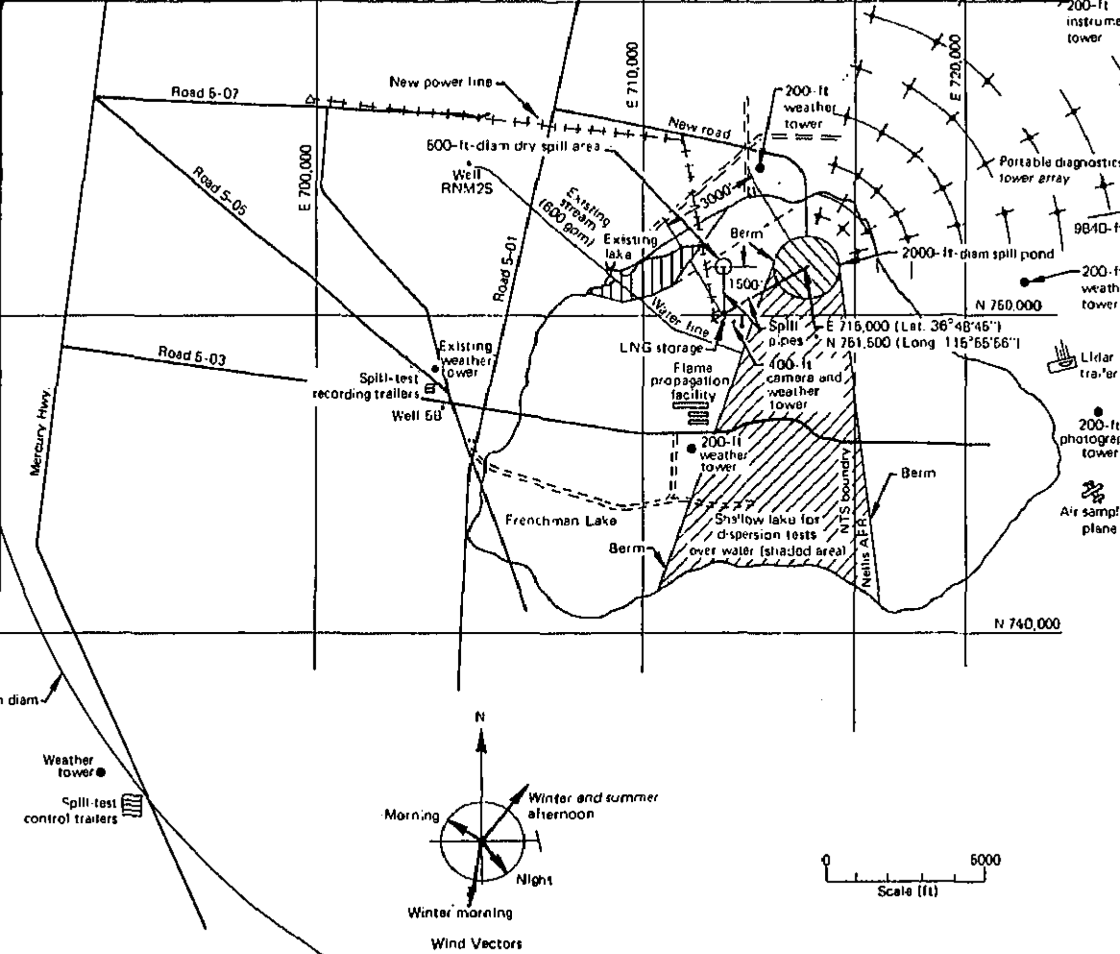


FIG. 6. Detailed map of the proposed LNG test installation at Frenchman Flat.

afe from the expected effects of the spill test ram.

The area east of the Nye county line is a game e which contains two threatened plant species. game range area has been proposed as a erness area in the future. LNG vapor dispersion will not damage the area, and planned burn will not be carried out in the area.

No interference is expected between the nuclear rogram and the LNG test program if the latter ated at the Frenchman Flat area. Minimal ex- l constraints are expected at this location.

3. **Acceptable Surface Winds.** Wind speed ds over five to six years indicate that the fre- cy distribution of wind speeds is broad enough ver the full range of desired conditions (see Ap- ix D). Analysis of the data indicates that light s (0 to 2 m/s) occur at least 25% of the time in arly morning hours. The medium wind condi- tions (3 to 5 m/s) occur 10 to 30% of the tim early morning (probably drainage winds with comitant stable lapse rate) and perhaps 40% early afternoon, usually flowing in the o direction (upslope with an unstable lapse High wind conditions (8 to 23 m/s) can be approximately 40% of the time in the aftern the spring and summer. In general it should very difficult to find the wind speeds requi

The wind direction data at Well 5B (w of Frenchman Flat) has been carefully studi the following general comments can be ma The seasonal wind directions, caused by the ment of large-scale pressure systems, are ge northerly in the winter and southerly in the s and (2) the smaller scale "mountain-valley tend to predominate if large-scale weather are absent. Buoyancy effects then cause a

wind reversal from southeasterly (upslope) during the day to northwesterly (downslope) at night.

The meteorologists have expressed a concern for achieving conditions at the Frenchman Flat location which will maximize vapor cloud travel. The necessary conditions are believed to be light winds with stable (inversion) atmospheric lapse rates. The concern is that the spill location is near the bottom of the basin where the drainage winds would tend to converge and might have a very short reach. This problem is to be investigated in detail by installing six meteorological stations there about December 1, 1978. One station will be on a tower 60 m above the ground, and the other five will be 10 m above the ground (see Appendix D).

A more detailed evaluation of this particular site would be required in order to actually plan the experiments. We believe the following general statement can be made, however: The wind direction will be sufficiently steady and predictable to permit reasonable design of field tests.

4. Flat Land. Frenchman Flat derives its name from the dry lake bed near the center of the area. Figure 5 shows the contours and local topography. The dry lake bed is roughly circular in shape and about 4 km in diameter. The bed itself is extremely flat. The area to the north of the lake bed is a gently sloping plain (~1.5%) for a distance of 6 km, at which point the land rises abruptly forming a ridge of steep low mountains which separate Frenchman Flat from the basins to the north. To the southeast the same condition exists except that the slope of the land is steeper and the hills are approximately 3 km from the center of the lake bed. To the west the ground gradually slopes 15% upward until it drops into Jackass Flats. The crest of the pass is about 18 km from the center of the lake and approximately 380 m above the lake bed elevation. A large flat area should be extremely easy to obtain at this location.

5. Wide Range of Atmospheric Conditions. The data source for atmospheric stability is Ref. 7. It is not extensive, but is sufficient to roughly indicate that the required range of stability conditions can be found at NTS. For example, it indicates that surface-based inversions can be expected between 80% (winter) and 96% (summer) of the time at 4 a.m. at Yucca Flat, with an average inversion depth of about 250 m. Similar conditions are predicted at Frenchman Flat. Since stable atmospheric conditions accompany these inversion conditions, we can expect frequent morning occurrence of Pasquill-Gifford stability categories E and F. At the other extreme, we can expect unstable

the desert (categories A and
speeds are moderate (3 to 5 m/s
expect near neutral (C-D) stabi
times: (1) during transition per
and unstable, (2) during cloudy
and (3) perhaps during the late
wind speed is high and the sola
ter two conditions are more a
plan and probably occur suffic

6. Large Body of Water.
body of water does not exist
however, during most years m
bed is covered with several inc
the winter and early spring mo
face quickly disappears as th
proaches. By selective schedul
spill tests, advantage can be ta
and wet conditions of the lake

7. Available Water Suppl
well was completed approxima
NW edge of the lake bed.
producing 600 gpm continuo
ber 1, 1977, as part of a study
derground migration of low-le
tivity resulting from an under
conducted several years ago. T
sidered by NTS to be contamin
and is currently draining into
Frenchman Lake where it is co
low dikes. The actual size of t
very dependent upon the wea
controls the evaporation rate.
cellent water source for a futu
are also four other wells just
with a capacity of over 10
capacity of about 1600 gpm.

8. Low Costs. The total
support a particular project
many things: design, constructi
tenance, and demobilization.
dependent upon location, ease
isting facilities, availability of c
port crews, availability of ma
logistics, etc. It would be beyo
report to attempt to projec
operating at Frenchman Fla
ticular site. However, it is t
engineers that Frenchman Fla
most economical of all the
vestigated. This judgment is ba
of many factors such as ease
conditions, existing roads, we
munications, existing labor fo
systems, etc. Overall, Frenc

g the winter months. These systems can be ast for several hours with good accuracy (by neteorologists at the NOAA Weather Support ce's Nuclear Support Office, Las Vegas) and be expected to supply rainfall at the 1-mm/hr for 3 to 6 hours. Heavy rains (~10 mm/hr), ever, should *not* be counted on at NTS (Yucca data indicate that 10 mm of rain in an hour will occur once in every 2.5 years at any specific ion). A reasonable approach would thus be to on a series of winter tests and take advantage e rainstorms that do occur. It is likely that lack gh rainfall rates will be found to be relatively portant.

10. Variable Topography. As mentioned ously this category is somewhat inconsistent flat lands if one is considering high relief.

Summary of Frenchman Flat. This area without its problems and difficulties; howeve of them are insurmountable. Most of the either be avoided by careful planning and sc ing or can be eliminated by various engineeri construction applications. The advanta Frenchman Flat far outweigh the disadva No site is perfect, and every one is a compro some aspects. This site ranks very high in t five categories: safety, minimal external cons acceptable surface winds, flat land, and wide of atmospheric conditions. It also ranks very category 8, low costs. In the four rem categories, Frenchman Flat is a compromise it is less than the best. Three of these cat would be a compromise in most desert locat large body of water, available water suppl rainfall.

IX. CONCLUSIONS AND RECOMMENDATIONS

We have developed a prioritized set of criteria electing a site suitable for experimenting with -scale LNG spills. These criteria are based our estimates of the characteristics of the ex- nents necessary to verify the analytical models accomplish the DOE's program goals.

Using the criteria developed, we have been able iminate from further consideration a large ber of sites originally contained in the list of dates (Ref. 1). Of the remaining sites, we note many of the more desirable ones have similar ral characteristics. They are large federally d facilities in desert areas of the West. The graphy and weather features of such sites are similar also. From the viewpoint of accom- ng the experimental goals of the program, fore, there may not be a strong preference ng many of the remaining sites. In this case of the nonexperimental site selection factors as safety and logistics arrangements can be to make a choice between sites, with con- ce that the selected site will be at least as good the experimental viewpoint as the sites passed Weighting some of those factors (for example, isting adequate EIS, and DOE ownership) can d result in more rapid progress on the program is found that existing administrative arrange- s can be used.

Such was the case in our decision to c trate our detailed site evaluation on the N Test Site. We clearly recognized that NTS had in common with the other Western desert sit as the Naval Weapons Center and Edwar Force Base. Some experimental criteria perhaps satisfied in a better way, while other not satisfied as well. For example, NTS has explicit and complete weather records tha other site considered. On the other hand, few desert sites contain permanent bodies of wat the whole, however, it is reasonable to say tha of the program's technical objectives probably be accomplished at any one of similar sites.

We found that NTS (and a portion of t rounding Nellis AFB) had a number of add features that combined to make it an attract for the LNG tests:

- Excellent record for safely hosting hazardous experiments.
- Local population of people who ha with this situation (i. e., conducting large, dous tests) for many years.
- An existing EIS which covers the program without alteration.
- DOE ownership.

ng convenient administrative arrangements.

• Detailed weather records and good predic- apability.

• Good control of possible test areas.

• Familiarity with operational procedures acking hazardous clouds.

• Convenient, rapid access by LLL person-

• Seasonal lakes.

• Surplus equipment which may save llion.

While some of the other desert sites had some ese additional features, none had them all. efore, we recommend that NTS be selected as te for location of the facility for the large-scale experiments.

within NTS has resulted in our conclusion t Frenchman Flat is the most desirable location. T site appears to offer the greatest flexibility in exp ment planning and may result in the smallest faci cost. Therefore we recommend that Frenchm Flat be selected as the planned location of facility. Work should proceed at once on tak more extensive weather data and other data at site to allow the detailed facility design effort proceed.

Administrative arrangements between L and the Nevada Operations Office, which ministers NTS, should be finalized as soon a practicable. Only if this detailed work uncove heretofore unseen obstacle would we recomm any further work on other candidate sites.

X. REFERENCES

Preliminary Site Criteria for LNG Scale Effects Experiments," Appendix G in *An Approach to L efied Natural Gas (LNG) Safety and Environmental Control Research*, Department of Ener Vashington, D.C., DOE/EV-0002 (1978).

Final Environmental Impact Statement, Nevada Test Site, Nye County, Nevada, Energy Research a Development Administration, Washington, D.C., ERDA-1551 (Sept. 1977), p. 3-33.

ee Ref. 2, p. 5-2.

V. C. O'Neal and W. J. Hogan, *Environmental Analysis for a Proposed Temporary LNG Spill Test Facility at Frenchman Flat*, Lawrence Livermore Laboratory, Livermore, Calif., UCID-17951 (to published).

M. Gates, letter to R. Wagner of LLL giving approval to consider the Nevada Test Site as a location he LNG spill-test facility, dated March 6, 1978. See Appendix F for a copy of this letter.

M. Gates, *Approval to Conduct Liquid Natural Gas (LNG) Spill Effects Tests at the NTS*, letter to Vagner of LLL, dated August 2, 1978. See Appendix F for a copy of this letter.

R. F. Quiring, *Summary of Inversion Statistics*, Air Resources Laboratory, Las Vegas, Nevada, ARL 51-37 (Jan. 1973).

Estimates of the downwind dispersion of LNG vapor were made using a formulation origina[...] meles and Drake.[1] This formulation is made up of three separate models which are only couplec[...] that one provides initial conditions for the next in the sequence in which they are applied: vapor [...] gravity spread of the vapor, and finally, downwind dispersion of the vapor. The selection of th[...] ar composite model was based on recommendations made by Jerry Havens of the University of A[...] ate communication) that it represented a "middle ground" assessment of the hazard associat[...] nwind dispersion. Details of the model may be found in the original paper by Germeles and Drake.

The model is capable of dealing with continuous or instantaneous spills. No comparison [...] nental results and model results has been made; however, such comparison is anticipated when dat[...] er scale LNG spills (5 m^3) have been collected at China Lake.

A brief description of the continuous spill model has been incorporated here for completeness [...] is section has been paraphrased from the Germeles and Drake paper or quoted directly.

The decoupling of the models is based on the following assumptions, which cause the ana[...] stimate the vapor travel.

As the LNG pool boils and spreads, the vapor it generates spreads without mixing so that it f[...] ylinder of pure cold methane over the entire LNG pool at the moment the last liquid vaporizes. N[...] ty spreading model treats the vapor cloud as a progressively growing cylinder, starting from an [...] s equal to the maximum liquid pool radius and expanding radially until the rate of spread becon[...] wind velocity. During the evaporation phase, all atmospheric turbulent mixing is neglected. Dur[...] ty spreading of the cloud, large-scale entrainment is accounted for using an entrainment coef[...] n the gravity spread velocity becomes less than the wind velocity, gravitational effects are assume[...] gible and all further dilution is assumed to be due only to atmospheric turbulence.

r Generation

For a continuous spill at a rate $\dot{V}$ (m^3/s), the maximum pool radius r_e is determined by the po[...] red to vaporize the LNG at a rate equal to the spill rate:

$$r_e\,(\text{meters}) = (\dot{V}/\pi W)^{1/2},$$

e W is the regression rate of the pool (m/s). An equivalent height of vapor for input to the [...] ading analysis is estimated as

$$h_e\,(\text{meters}) = 0.21\,(r_e/U),$$

e U is wind speed (m/s).

Gravity Spreading Model

After pool evaporation is complete, the resultant vapor cloud is assumed to be a flat cylind[...] g mostly of cold methane vapor. Its gross shape is characterized by an average radius R and an [...] ness H. Initially, $R = r_e$ and $H = h_e$ as derived from the evaporation model. As the cloud spr[...] ity, both the heating and dilution of the cloud by the environment will vary locally; i.e., the instant[...] nodynamic state of the cloud will have some radial and vertical gradients. However, in this mo[...] d is represented only by its average spatial thermodynamic state, a state which is spatially unifo[...] h varies with time. The spread equation gives the variation of the cloud radius with time:

$$\frac{dR}{dt} = \left[2g\left(\frac{\rho - \rho_a}{\rho_a}\right)H\right]^{1/2},$$

e g is the acceleration of gravity, ρ the cloud density, and ρ_a the density of ambient air.

$$Q_e = \frac{2\pi}{3} \cdot \alpha R^2 \frac{dR}{dt} .$$

The entrainment coefficient α is selected to be 0.1 on the basis of an extrapol experiments involving the flow of a layer of fresh water over a layer of salt water. [2]

Mass and Energy Conservation

Mass and energy conservation equations are next derived. Air entrainment the cloud: dilution and heating. The latter effect is primarily due to air entrainment ra tion and freezing of water vapor contained in the air. The cloud is also heated by conv ground surface beneath it.

Mass conservation for the cloud is

$$\frac{dM}{dt} = \rho_a \; Q_e \; ,$$

and energy conservation is

$$\frac{d}{dt} (cMT) = c_a \rho_a Q_e T_a + Q_v + Q_w \; ,$$

where c, M, and T are respectively the cloud's specific heat, mass, and temperatur specific heat and density of the ambient air. The heat transfer rates Q_v and Q_w accoun tent heats of condensation and freezing of water vapor and for the heat transfer from boundary.

The value of Q_v depends on the moisture content in the air and on the temp itially, when the cloud is very cold, all the water vapor contained in the entrained air c the cloud warms up and becomes able to hold water vapor, some of the entrained w dense. Consequently, Q_v diminishes per additional unit volume of entrained air. Fina tions, it is possible that, before neutral buoyancy is achieved, the cloud temperatur such that not only does none of the newly entrained water vapor condense but also condensed water vapor re-evaporates (Q_v is now negative).

The heat transfer from the water surface, Q_w, is a combined effect of natura but the combined effect is not directly included in the model. Instead, the heat trans convection, Q_n , and pure forced convection, Q_f , are computed individually and Q_w i Q_f, whichever is larger at any given time in the cloud's development.

Analytical Model for Atmospheric Dispersion

After the gravitational spreading of vapor has been determined, the general and its mean concentration are known. Now the cloud is assumed to be near enoug that the usual analyses for dispersion of atmospheric pollutants are employed.

In particular, for continuous spills or for those that persist long enough which are elongated in the direction of the wind, a continuous, finite line source trans

$$C(x,y,z,t) = \frac{\dot{Q}}{UL} \sqrt{\frac{2}{\pi}} \frac{1}{\sigma_z} \left[\exp\left(- \frac{z^2}{2\sigma_z^2} \right) \right] \theta_L \; ,$$

$$\theta_L = \frac{1}{2} \operatorname{erf}\left(\frac{L/2 - y}{\sqrt{2}\sigma_y}\right) + \operatorname{erf}\left(\frac{L/2 + y}{\sqrt{2}\sigma_y}\right),$$

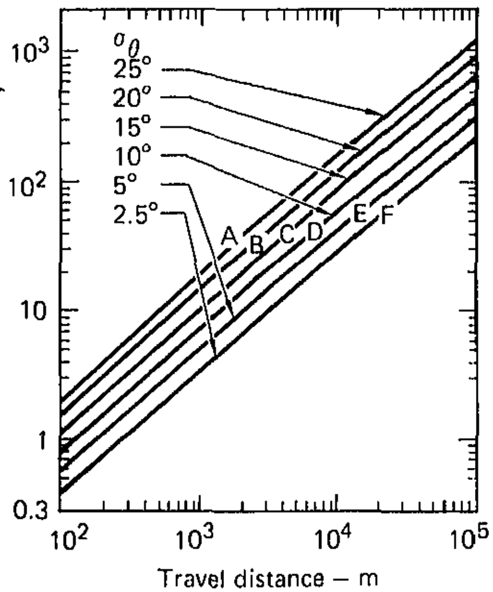
C = gas concentration (average); x,y,z, = distance coordinates from a virtual line source located at ... time from release; $\dot{Q}$ = source generation rate; U = wind velocity; L = width of line source (equ... d width at end of gravity spread); and σ_y and σ_z = dispersion coefficients. In this model, the va... med to be released from a virtual line source located at a distance x_v upwind of the actual spill locatio...

The calculations made for siting evaluations are based on a set of wind speeds and ... esponding Pasquill-Gifford stability categories. The values used for the lateral/longitudinal and th... l dispersion coefficients were obtained from the curves shown in Figs. A-1 and A-2. These figures also ... guidance for the selection of the stability category depending on the wind speed and on the day or ... ditions which may exist. The relative humidity was selected as 65% in all cases and the air and surface ... ature were 288°K. The spill rate selected was 8.3 m^3/s, corresponding to a spill of 1000 m^3 of liqu... inutes.

Tables A-1 and A-2 summarize the results. Table A-1 contains the results of vaporizatio... ity spread, and Table A-2 shows the maximum downwind distances to mean concentrations of 15%... er flammability limit, UFL), 5% (the lower flammability limit, LFL), 2.5%, and 0.25%. These las... es correspond to concentrations which are respectively lower by factors of 2 and 20 than the LFL. ... e been included to address the question of ratios of peak to mean concentration of 2 to 1 and 20 ...

An important factor to consider in looking at these results—particularly, the long travel distan... 0.25% case—is that these conditions must persist for the duration of the dispersion. This is unlikely ... of a very stable atmosphere as daytime insolation increases. These results do, however, give guidan... esirable conditions in which to spill volumes of 1000 m^3 or more.

Horizontal dispersion coefficients



Relation of Pasquill turbulence types to weather conditions

Pasquill turbulence types
- A—Extremely unstable
- B—Moderately unstable
- C—Slightly unstable
- D—Neutral*
- E—Slightly stable
- F—Moderately stable

*Applicable to heavy overcast, day or night.

Surface wind speed (m/s)	Daytime insolation: Strong	Moderate	Slight	Night conditio...: Thin overcast or cloudiness ≥4/8	Clo... ≤...
2	A	A-B	B	–	
2	A-B	B	C	E	
4	B	B-C	C	D	
6	C	C-D	D	D	
6	C	D	D	D	

†Cloudiness is defined as the fraction of sky above the local apparent horizon that is covered by clouds.

FIG. A-1. Pasquill horizontal dispersion coefficients.

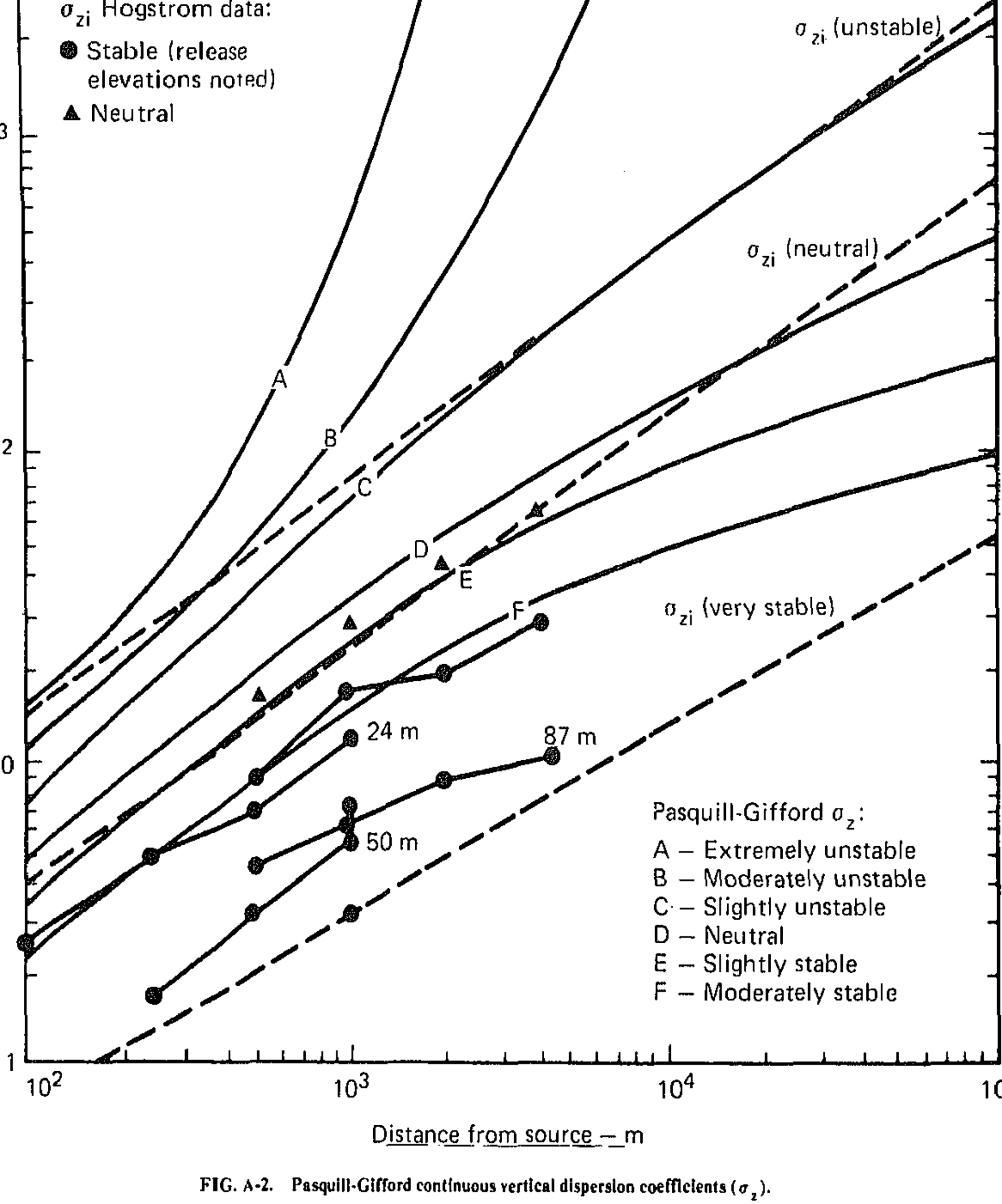


FIG. A-2. Pasquill-Gifford continuous vertical dispersion coefficients (σ_z).

LE A-1. Model results for a 1000-m^3 LNG spill, assuming a spill time of 2 minutes and an air temperatu
88°K.

		Cloud conditions at end of vaporization				Cloud conditions at end of gravity spread			
e	Wind speed (m/s)	Radius (m)	Height (m)	Time (s)	CH_4 (%)	Radius (m)	Height (m)	Time (s)	CH_4 (%)
	2	79.5	8.3	120	100	171	7.2	138	67
	5	79.5	3.3	120	100	137	7.5	128	82.5
	10	79.5	1.7	120	100	79.5	1.7	120	100

Wind speed (m/s)	Stability category (Pasquill-Gifford)	Downwind distance (m) to CH_4 concentration of:			
		15% (UFL)[a]	5% (LFL)[b]	2.5% (2/1)[c]	0.25% (20
2	F	5016	13,140	22,790	136,400
5	B	171	461	720	2,391
10	D	444	1,214	1,958	8,287

s the upper flammability limit, at 15% CH_4 concentration.
s *the lower flammability limit, at 5% CH_4* concentration.
the LFL dispersion (i. e., half the LFL concentration).
y times the LFL dispersion (i. e., one-twentieth the LFL concentration).

es

E. Germeles and E. M. Drake, "Gravity Spreading and Atmospheric Dispersion of LNG Va
ıds," paper presented at Fourth International Symposium on Transport of Hazardous Cargoe
and Inland Waterways, sponsored by U.S. Department of Transportation (U.S. Coast Gua
sonville, Florida, October 26-30, 1975.

.ofquist, "Flow and Stress Near an Interface Between Stratified Liquids," *Phys. Fluids* 3, 158 (196

LNG VAPOR-CLOUD DETONATIONS

by Steve Sutton

In the past 40 years numerous accidental releases of hydrocarbon fuels have occurred in wl ficant damage has resulted from detonation of the cloud of dispersed fuel. Our present concern is that emplated large shipments of LNG could lead to large spills followed by catastrophic explosions. It found that methane is difficult to detonate, which tempts one to hypothesize that the explosion da ciated with a cloud of unconfined methane in air may be slight. However, this hypothesis has not ied, and therefore in making safety analyses of the LNG spill tests one must assume that detonation r. The following is a discussion of the methods used to predict the overpressures resulting fro othetical explosion of an LNG vapor cloud.

Two methods are frequently used to predict overpressures from fuel cloud detonations: (1) a nding historical observations to predict the explosive yield, (2) assume a pressure state at the edge wn cloud configuration to estimate the explosive yield. For purposes of this study, we have elected to method 1 since it should provide an upper bound.

Strehlow[1] and Strehlow and Baker[2] give good summaries of the historical origin of method ıld be regarded as an after-the-fact approach using real accidents. Accident scenes are surveyed anc nage pattern catalogued. Then this damage pattern is used to determine the weight of HE (high explo ired to do the observed damage. The percent yield of the spill is then determined by calculating the we spill that would have the same combustion heat release as that amount of HE, and then taking centage of this calculated spill weight to the actual spill weight. Historically this value lies in the range % to 16%. Strehlow[1] states that the 16% value was for a proven detonation, while the highest obse agration yield was about 10%.

It should be noted that this method in no way attempts to account for exact cloud configuratio ct volume of fuel within combustible limits. The percent yield is based on the total spill volume or we wever, both of these factors are statistically embedded in the equivalent yield factor.

The accidents surveyed traditionally involve fuels such as butane and propane. Historically, s detonate much more readily than natural gas, thus they have a greater damage potential. However, i tulates that a methane detonation can occur, this approach should be acceptable for use on met uds since the detonation parameters and energy release of methane are very similar to those of propane

Application of this technique allows one to determine what might be called the statistically bable damage. The approach is to predict the explosive yield using the equation

$$\text{HE equivalent (lb)} = \frac{\epsilon \cdot V \cdot \Delta H}{2000} ,$$

ere

ϵ = percent yield ($\leqslant 16\%$),
V = volume of fuel within the combustible limits (ft^3),
ΔH = combustion energy (Btu/ft^3)
= 1150 Btu/ft^3 vapor (for natural gas).

Then, an overpressure curve for HE (Fig. B-1) can be applied to predict the pressure pattern. Re summarized in Figs. B-2 and B-3. In Fig. B-2, the yield as a function of spill volume is given. In thi nce we have assumed a 16% yield factor, which is regarded as a conservative assumption (i.e., on the e). In Fig. B-3, the range at which the shock wave will dissipate to a particular value is given as a functi lled liquid volume.

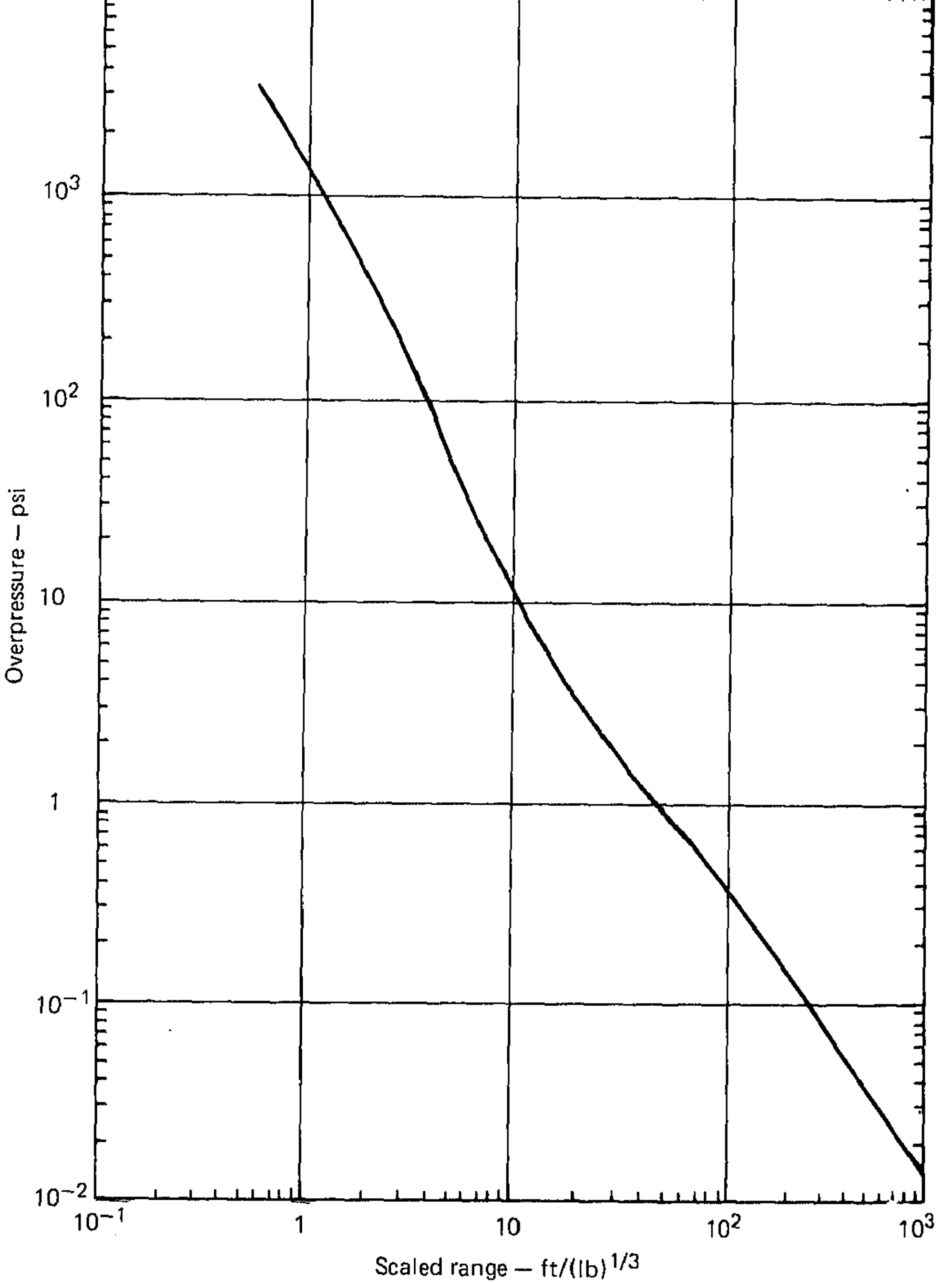


FIG. B-1. Overpressure vs scaled range for an HE detonation.

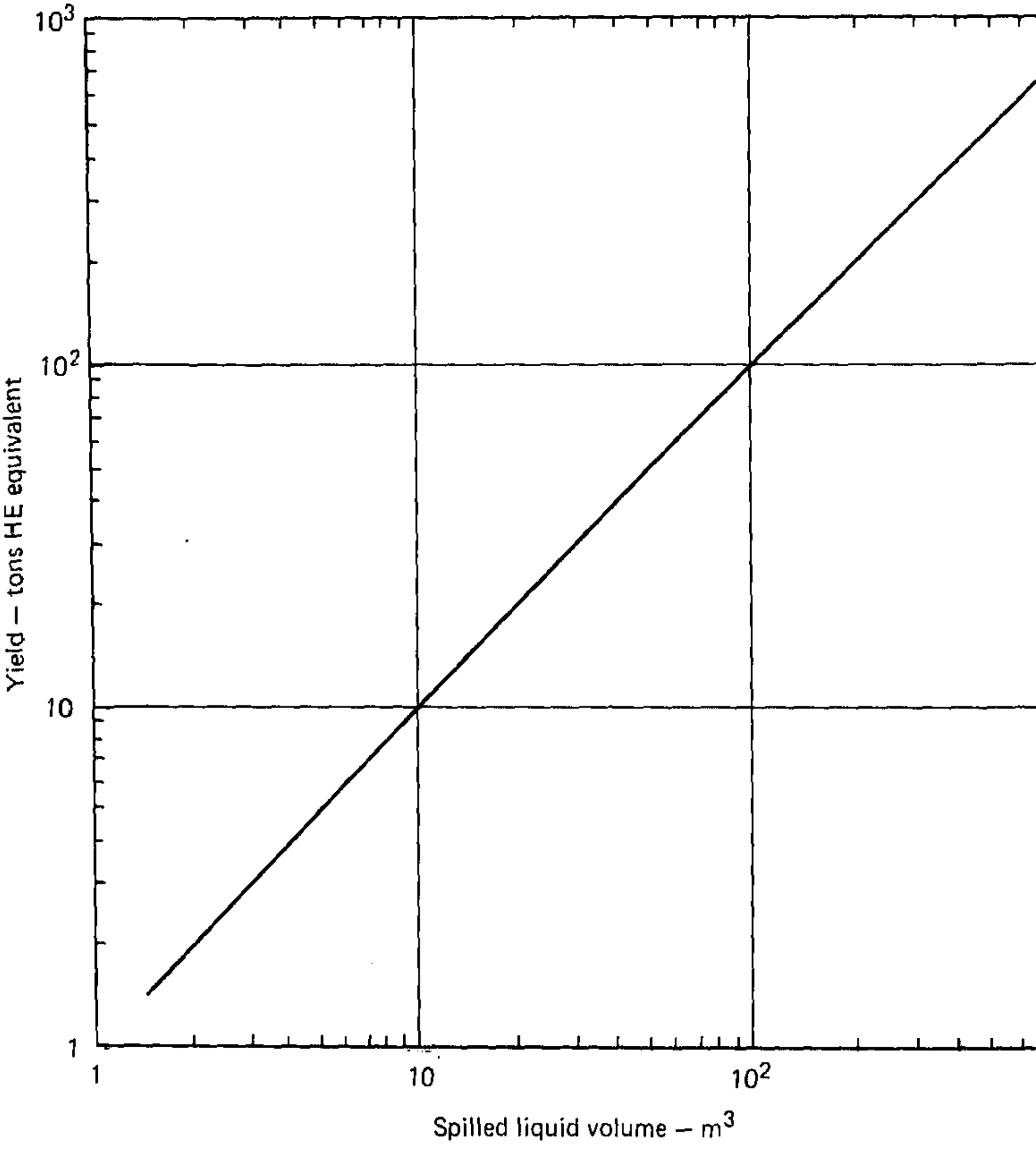
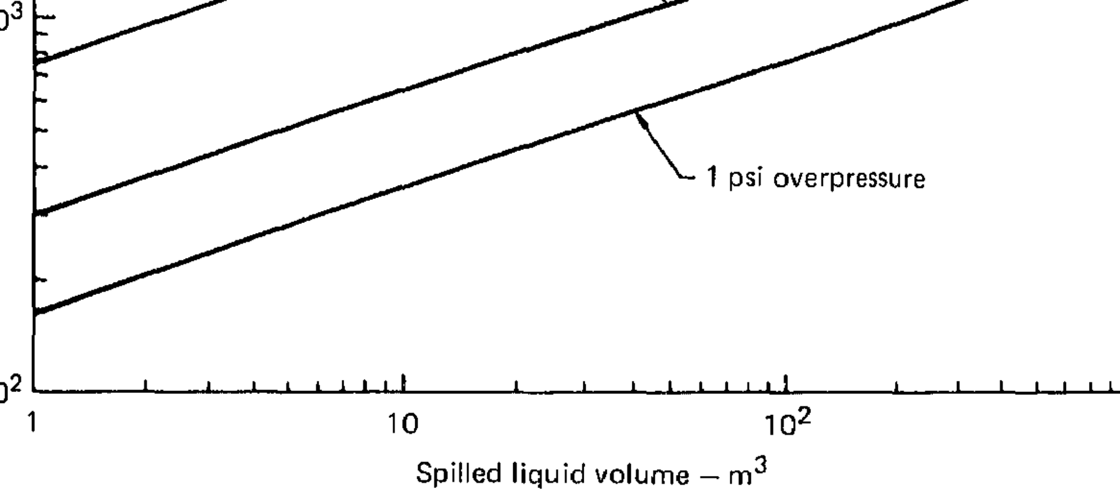


FIG. B-2. Explosive yield of vaporized LNG as a function of the spilled volume of LNG, assuming a 16% equivalence factor (l
plosive yield of the LNG is 16% of what would be calculated for it on the basis of its combustion heat release).



3. Overpressure ranges for detonated LNG vapor as a function of the spilled volume of LNG, assuming a 16% equivalence fa

From these results we conclude that if a detonation occurs in a 1000-m^3 LNG spill test the expl
vill be less than that produced by 919 tons of TNT. This could cause window breakage (assuming a
eakage threshold) out to a distance not greater than 1600 m. (This projection assumes that the clo
pherical. For clouds of other shapes, the distance from the cloud center to the limit of window brea
be 1600 m plus the actual cloud radius minus the hemispherical-assumption radius.)

ences

. A. Strehlow, "Unconfined Vapor Cloud Explosions—An Overview," in Proceedings of the 14th C
stion Symposium, 1972 (LLL LNG File A-45).
. A. Strehlow and W. E. Baker, "The Characterization and Evaluation of Accidental Explosio
rogress in Energy and Combustion Science, Vol. 2, pp. 27-60 (1976).
N. Bradley, *Flame and Combustion Phenomena* (Methuen, London, 1969).
runo J. Zwolinski and R. C. Wilhoit, "Heats of Formation and Heats of Combustion," in *America*
tute of Physics Handbook (McGraw-Hill, New York, 1972), p. 4-316 ff.
. A. Decker, "An Analytical Method of Estimating Overpressures from Theoretical Atmospheri
osions," presented at 1974 Annual Meeting of the National Fire Protection Association, May 23,

by W. M. Porch

This appendix describes results of a worst-case analysis of the nuclear radiation hazard associ
n possible LNG vapor detonation over a contaminated area in the region of Frenchman Flat.

The analysis assumed the maximum possible ^{239}Pu resuspended from the ground combined wit
spheric conditions which transport and deposit the highest concentrations to the surface. The assu
ditions for dust suspension were the following:

1. Largest possible detonation (equivalent to 6 kt HE).
2. The same amount of dust lifted from the surface as was produced from nuclear and higl
sive tests over Frenchman Flat with 6 kt yield.
3. Detonation taking place over a 600-m-diam area with the highest ^{239}Pu specific activity fou
previous soil surveys of the area.

The estimate of detonation yield is based on the total energy available from 1000 m^3 of LNG
ed in Appendix B, this is a very conservative assumption. The dust lofted from this yield is based o
sive tests at the Nevada Test Site.[1] These data show that the lofted dust expected from a 6-kt explosio
about an hour) can be as much as 2000 tons. The cloud top is estimated to be 7 km high with a horizo
meter of 2 km. Knowing the total dust lofted and choosing an area in the Small Boy regions of French
t with the highest average specific activity in a 1975 survey, we can determine the ^{239}Pu content of the c
ve assume that the specific activity of the dust in the air is the same as on the ground (10 nCi/g). Thi
es that a 1000-m^3 LNG spill may loft a cloud containing as much as 20 Ci of ^{239}Pu. After generatin
ud in this way, we chose atmospheric conditions which would transport the most material to the grou
e the highest air concentration and surface deposition. To get the highest surface air concentration
ove the surface), the following conditions were assumed:

1. No rainout of material.
2. Unstable upper air (Pasquill-Gifford stability B).
3. Winds of 5 m/s, unvarying with height (no shear).

get the highest surface deposition the following conditions were assumed:

1. High rainout and rain rates (25 to 100 mm/hr).
2. Rain beginning soon after the cloud leaves the test area.
3. Winds of 5 m/s, unvarying with height (no shear).
4. Neutral stability.

nsport and Diffusion Model

The worst-case assumptions above were then used as input to a computer code called PATRIC.
e is a transport and diffusion code designed to calculate the three-dimensional distribution of atmospl
lutants in a given space- and time-varying flow field. It is based on the particle-in-cell model in whicl
ss or activity of the important species to be traced is represented by the spatial distribution of a large r
of marker particles. The temporal evolution of this particle distribution results from the transport of
ividual marker particle due to advection by the mean wind and diffusion by the Gaussian formula.
e is capable of computing instantaneous or time-integrated air concentrations and deposition wit
hout rainout for a variety of instantaneous or continuous sources, including inert and radioa
terials.

ults

The results of these calculations are shown in Figs. C-1 through C-4. In each of these fig
rizontal isopleths of integrated concentration (air or surface) are plotted assuming an initial vertical cor
ion profile, as shown in the insert, with 20 Ci total activity. The integrated air concentration show

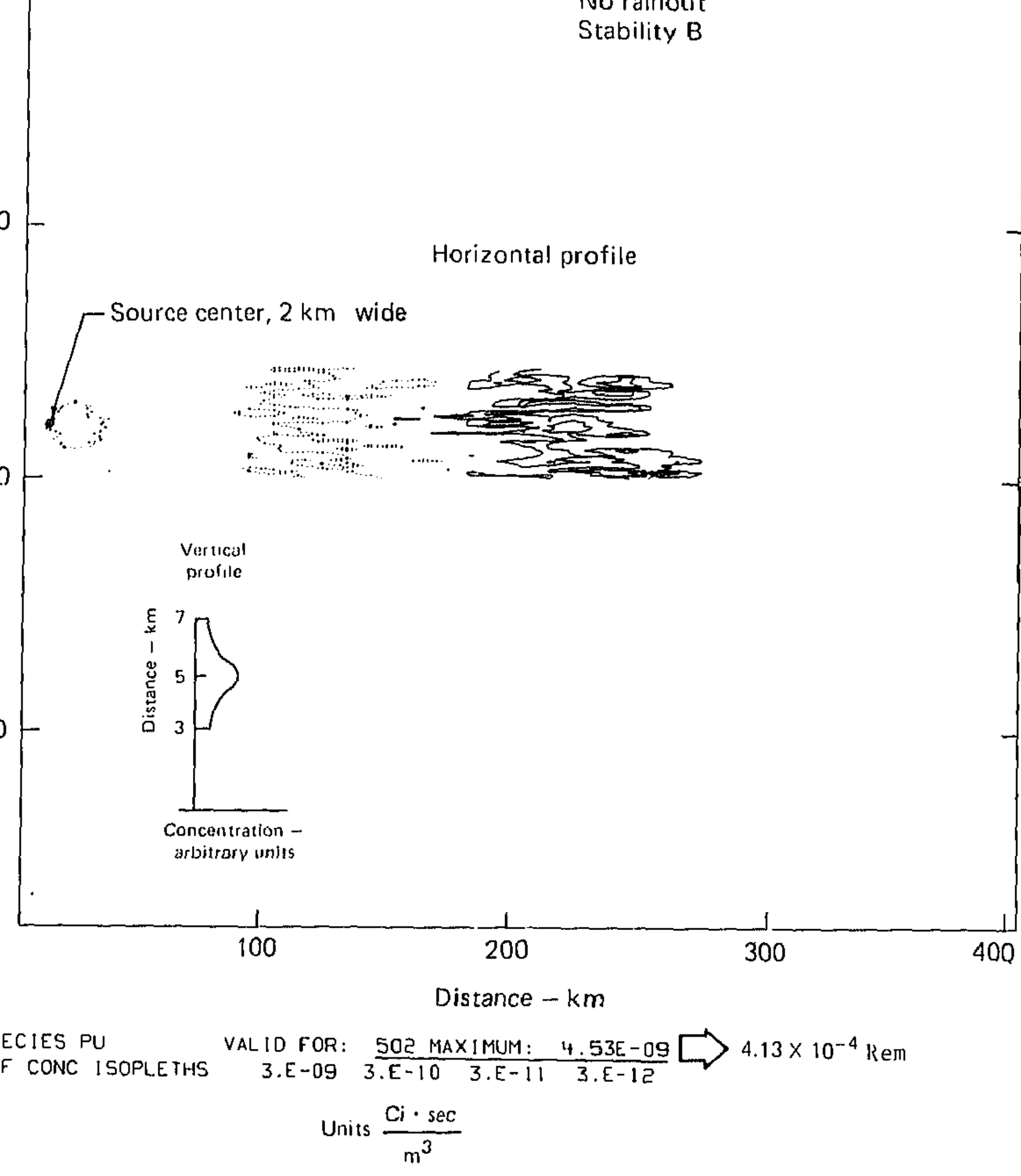


FIG. C-1. Integrated surface air concentration of ^{239}Pu calculated with the PATRIC code.

vas determined at a height of 3 m. The resultant maximum concentration was 4.53×10^{-9} Ci·s/m^3. dose conversion factor for ^{239}Pu of 3.3×10^{-4} rem·m^3/pCi·hr, this implies a total internal lung .13 $\times 10^{-4}$ rem. The surface deposition from this detonation with no rainout and monodisperse 1 μm radius is shown in Fig. C-2. The maximum value of 4.41×10^{-11} Ci/m^2 is negligible compared e where rainout is assumed. Figures C-3 and C-4 show the results of calculations where rainout was o occur, with rainout rates of 10^{-3} and 10^{-2} respectively. These rainout rates are associated with rain 5 and 100 mm/hr, respectively. The maximum surface concentration with a rainout rate of 10^{-3} was $^{-6}$ Ci/m^2. The maximum for a rainout rate of 10^{-2} was 3.16×10^{-6} Ci/m^2.

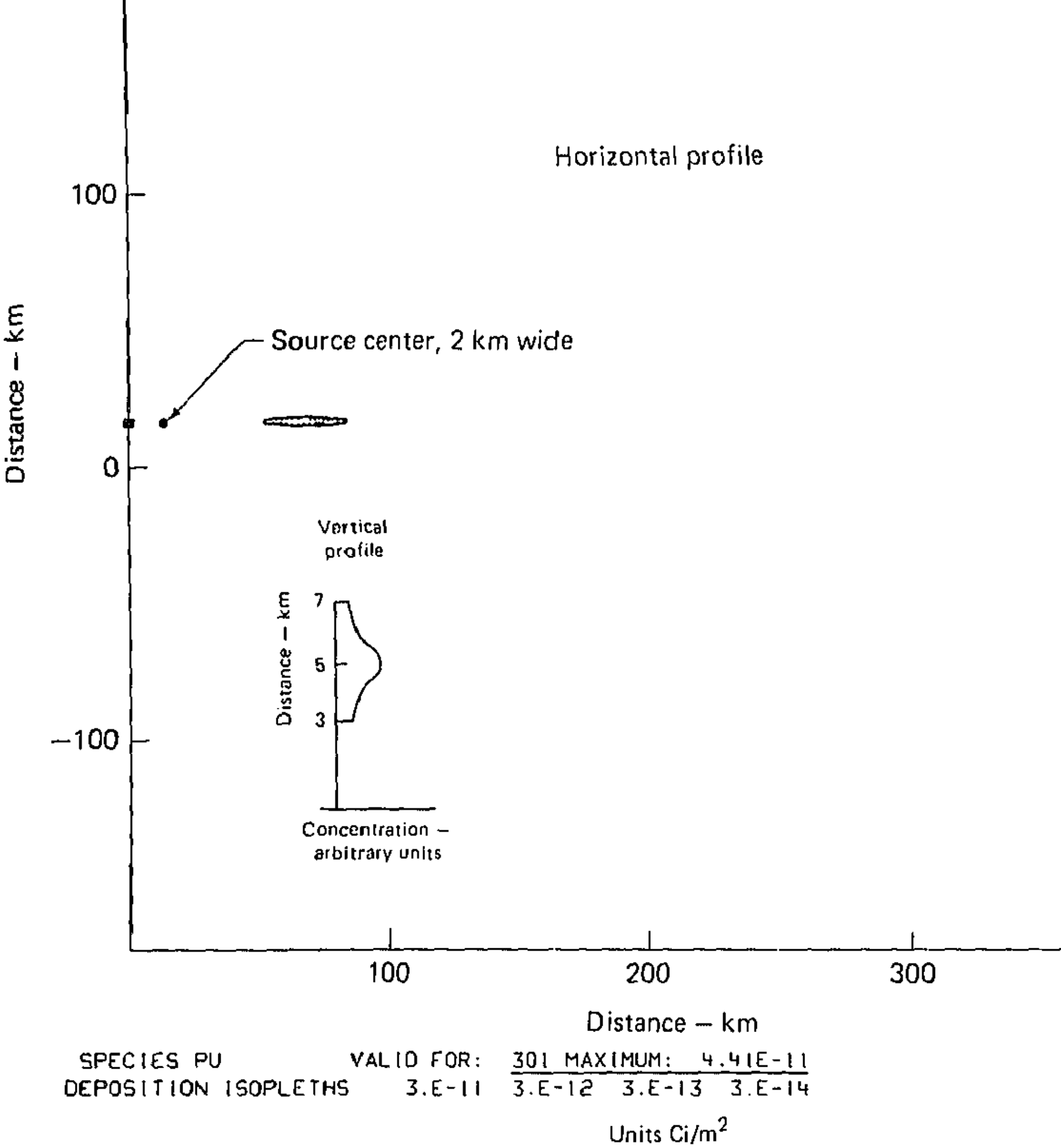


FIG. C-2. Integrated surface deposition of ^{239}Pu calculated with the PATRIC code.

Comparison with Standards for ^{239}Pu

These maximum values can be compared with standards and proposed standards for ^{23} based on internal lung burden in rems with the dose conversion given above. The LLL standard for uncontrolled situations. This standard is derived from Document Number 0524 of Standar tion Protection (1975). The Environmental Protection Agency (EPA) has proposed a much str for ^{239}Pu (Federal Register, Volume 42, Number 230, November 30, 1977) of 1 mrad or 10 maximum concentration associated with the assumptions used to derive the results in Fig. C-1

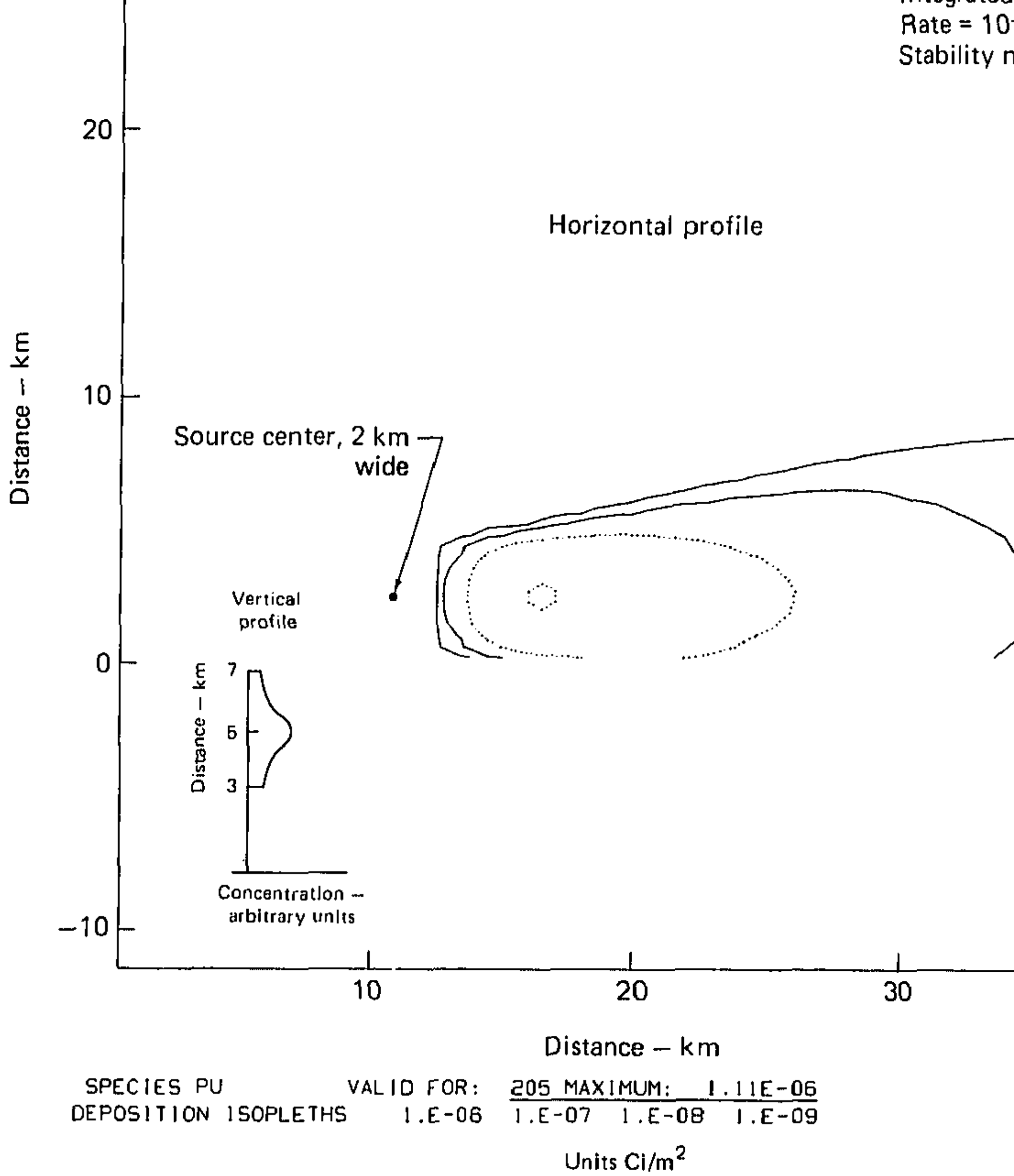


FIG. C-3. Integrated rainout of ^{239}Pu calculated with the PATRIC code, assuming a rainout rate of 10^{-3}

24 below this and occur less than 20 km from the source. This would be within the NTS/N area.

Proposed standards for surface deposition of ^{239}Pu vary from 0.2 to 0.8 μCi/m^2. The of 0.8 μCi/m^2 comes from Ref. 3. The stricter level of 0.2 μCi/m^2 is a standard proposed by E document. These standards would be exceeded for the assumptions used to derive the re Figs. C-3 and C-4 by factors of 1.4 to 16.0. However, the latter occurs only for weather condit likely to test in, and both occur only if the deposition occurs before significant dispersal of the mosphere (i.e., the debris is simply "moved" to another nearby location within the contro

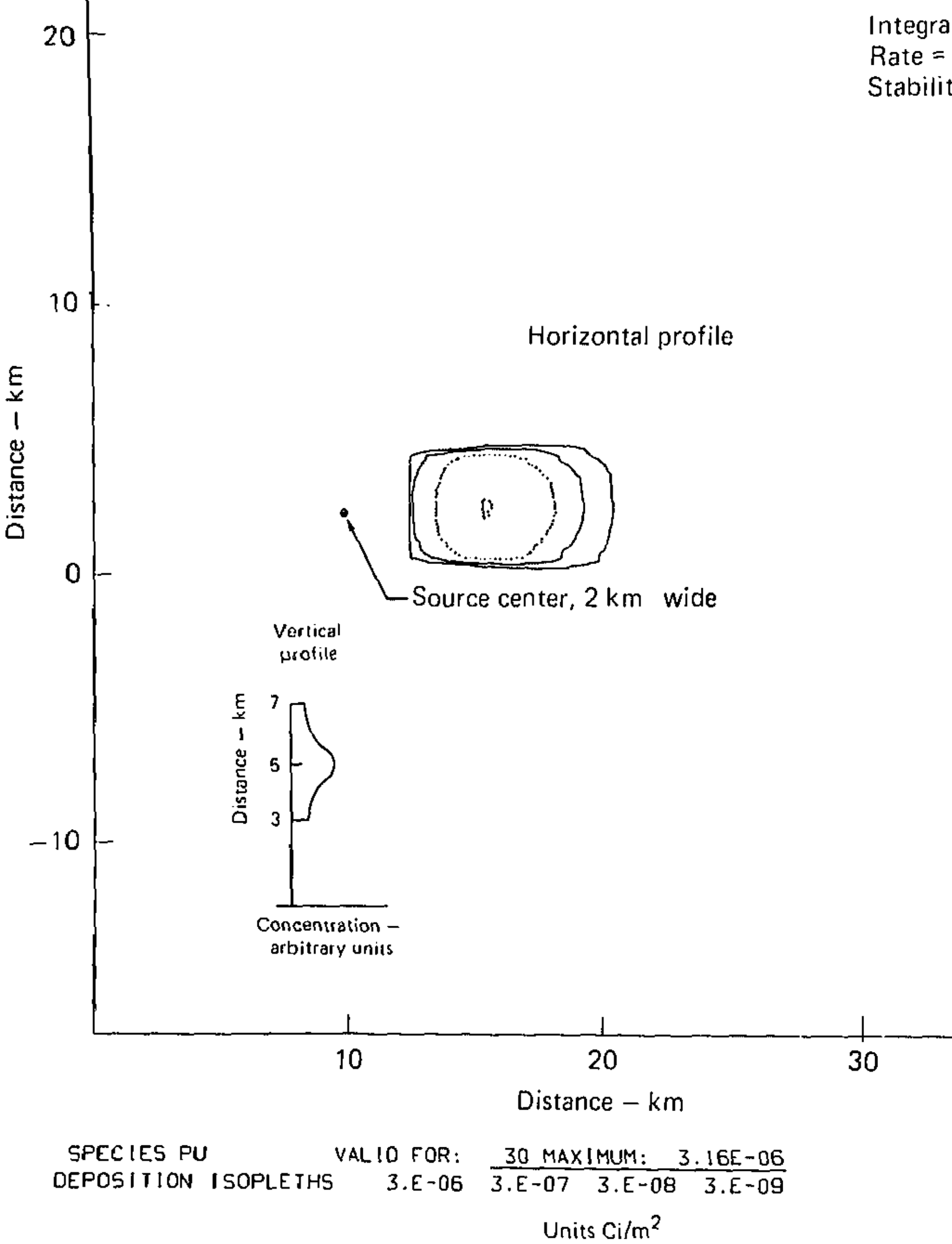


FIG. C-4. Integrated rainout of ^{239}Pu calculated with the PATRIC code, assuming a rainout ra

Discussion

These results show that the assumptions of worst-case dust suspension and atm lead to surface and air concentrations which are close to or exceed current and proposed within the controlled area. The following are reasons, however, which strongly sugg assumptions are too conservative:

1. Detonation rather than burn was assumed to simulate the dust from a 6-kt e ditions are far more likely. The dust lifted in a burn situation is not shaken from the groun orders of magnitude less dust suspended.

ewhat more spread in the rainout deposition pattern.

4. It is unlikely that a cloud at this height would experience no wind shear to spread its horiz
nt.

5. The highest average specific activity of the surface over a 600-m-diam detonation (10 nC
dominated by one measurement of 95 nCi/g, with no other measurement greater than 5.2 nCi/g ap
in the grid. This one "hot spot" could be removed if necessary.

There are also some reasons to suspect that our assumptions are not conservative enough:

1. The 2000 tons of dust associated with the 6-kt explosions was determined from air concent
surements taken some time after the explosion, and hence could be an underestimate of the total

2. Higher surface specific activities, though not likely, could have been missed in the surv

3. Models distribute activity evenly in grids, and "hot spots" are not included.

4. Convective clouds can bring distributed radioactive clouds together and focus the radioac
a smaller area.

5. Finally, these calculations do not include the effect of repeated surface burns and explosio
face erodability. A large increase in surface erodability of contaminated soil could lead to much mo
from subsequent high winds and dust devils than from the burns and explosions themselves. C
ies of suspension and soil erodability of ^{239}Pu for small-scale LNG experiments should be included
gram, and convective rain situations during tests should probably be avoided.

erences

R. G. Gutmacher and G. H. Higgins, *Total Mass and Concentration of Particles in Dust Clouds*, Law
Livermore Laboratory, Livermore, Calif., UCRL-14397 Rev. 1 (1965) (title U, report SRD).

R. Lange, *PATRIC, A Three Dimensional Particle-in-Cell Sequential Puff Code for Modeling the Tra
and Diffusion of Atmospheric Pollutants*, Lawrence Livermore Laboratory, Livermore, Calif., U
17701 (1978).

J. W. Healy, *A Proposed Interim Standard for Plutonium in Soils*, Los Alamos Scientific Laborator
Alamos, N. Mex., LA-5483-MS (1974).

Predicting a certain wind condition at Frenchman Flat on a specific date months ahead is imp... but through the use of the attached figures one can determine the most probable period in which ...ditions would be ideal for a specific test. Data for the attached figures (Figs. D-1 through D-11, at the ...his appendix) was collected from January 1970 through February 1978.

...rnal Wind Shifts

The best example of diurnal wind shifts is demonstrated by the month of September in Fig. D-...n vector wind. Topographical features of the terrain in the vicinity of the weather tower have the bi...uence on the diurnal wind shifts. There is a large drainage area, Mid Valley, with a somewhat restr...ning northwest of the tower site. A second large drainage area, Nye Canyon, is northeast of the tower ... the canyon gradually opens up as it proceeds southwest. All the other slopes are relatively small ...uld not contribute significantly to the diurnal wind shifts. After sunset the prevailing winds die an... ...pe to the northwest cools more quickly than the Nye Canyon slope. Shortly after midnight, the downs... ...ds from the northwest become effective and predominate. It can be noted from Fig. D-9 that from ...ht to 6 a.m. there is an equal chance that the wind will be either from the north or the southwest; and ... D-3 the wind constancy is seen to be approximately 20% for the same period. After sunrise the Mid V... ...a heats up first and the downslope winds from the Nye Canyon area to the northeast of the weather t... ...ome more prominent. Then, as the day progresses, the prevailing winds build up and predominate. ...stancy during this period is 10 to 20%. There is a 3 to 7% chance that the wind will be from the ea... ...theast during the transitional period. As pointed out in Ralph Quiring's article titled "Climatolo... ...ta, Nevada Test Site and Nuclear Rocket Development Station," this diurnal oscillation reaches its ...um amplitude in the summer.

...lms and Average Wind Velocity

The figures for calms (Fig. D-11) and for average wind speed (Fig. D-2) are self-explanator...

...nstancy

Wind constancy for Frenchman Flat is shown in Fig. D-3. An explanation of constancy of the ... ...uoted below from Ralph Quiring's article referred to earlier.

> "Constancy of the wind is expressed as the percentage ratio of the mean vector wind speed to the mean scalar speed. These charts give a relative measure of the variability of the wind on a scale from 0 to 100. If the wind distribution were absolutely symmetrical (same frequency and average speed from opposing directions), the constancy would be zero. On the other hand, if the wind always blew from the same direction, the constancy would be 100. These extremes are rare. However, if the constancy charts are examined in conjunction with the wind direction frequency charts, one can readily see that high values of constancy are associated with a tendency for the wind direction to cluster about a preferred direction. In contrast, with low values of constancy, there is either no preferred direction or possibly a preference for two opposing directions."

...rface Wind Summary

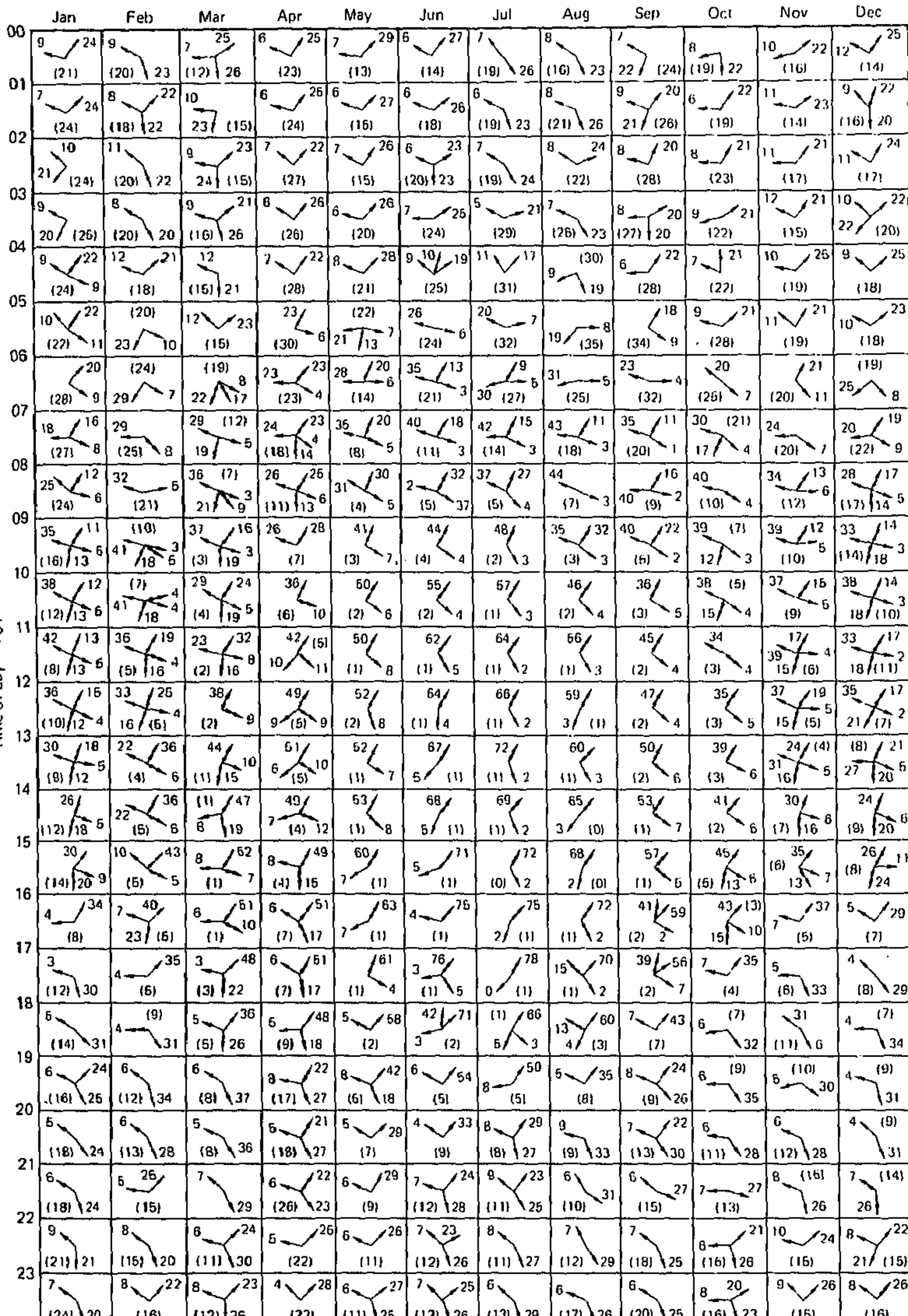
These charts show the maximum probability and minimum probability of wind direction for ...en hour of the day in each month of the year.

If the proposed tower is placed near the northeast portion of Frenchman Lake, there is a chan
ld observe that the Nye Canyon Basin would have a larger influence on the diurnal wind direc
etation and the lake bed's high reflectivity also can influence diurnal winds.

After the tower is erected and operating, it can record wind data on the same basis as SYST
ion 15, and the data from the two stations can be compared. In time, the terrestrial influences betwe
stations should be manifested. From this data, placement of portable weather towers can be conside
r to obtain more detailed information of wind patterns throughout the proposed dispersion are

s for Collecting Weather Data

Figure 6 earlier in this report (see Section VIII) shows the proposed locations of the new weath
s at Frenchman Flat. *Starting in December 1978 we will characterize the weather in the Frenchma
n using the new four-level 60-m-high tower, the existing 10-m single-level tower at Well 5B, and fi*
g portable 10-m single-level towers. Wind flow patterns during inversion conditions and unstable
s will be mapped, and horizontal and vertical wind speed, direction, and turbulence will be mea
se rate, humidity, barometric pressure, and rate of rainfall will also be measured. All data will be rec
ape, and the data from the 60-m tower will also be recorded on digital printers. The heat exchange be
existing shallow pond and the boundary layer above the water will be characterized by using standard
ient and energy-budget micrometeorological methods.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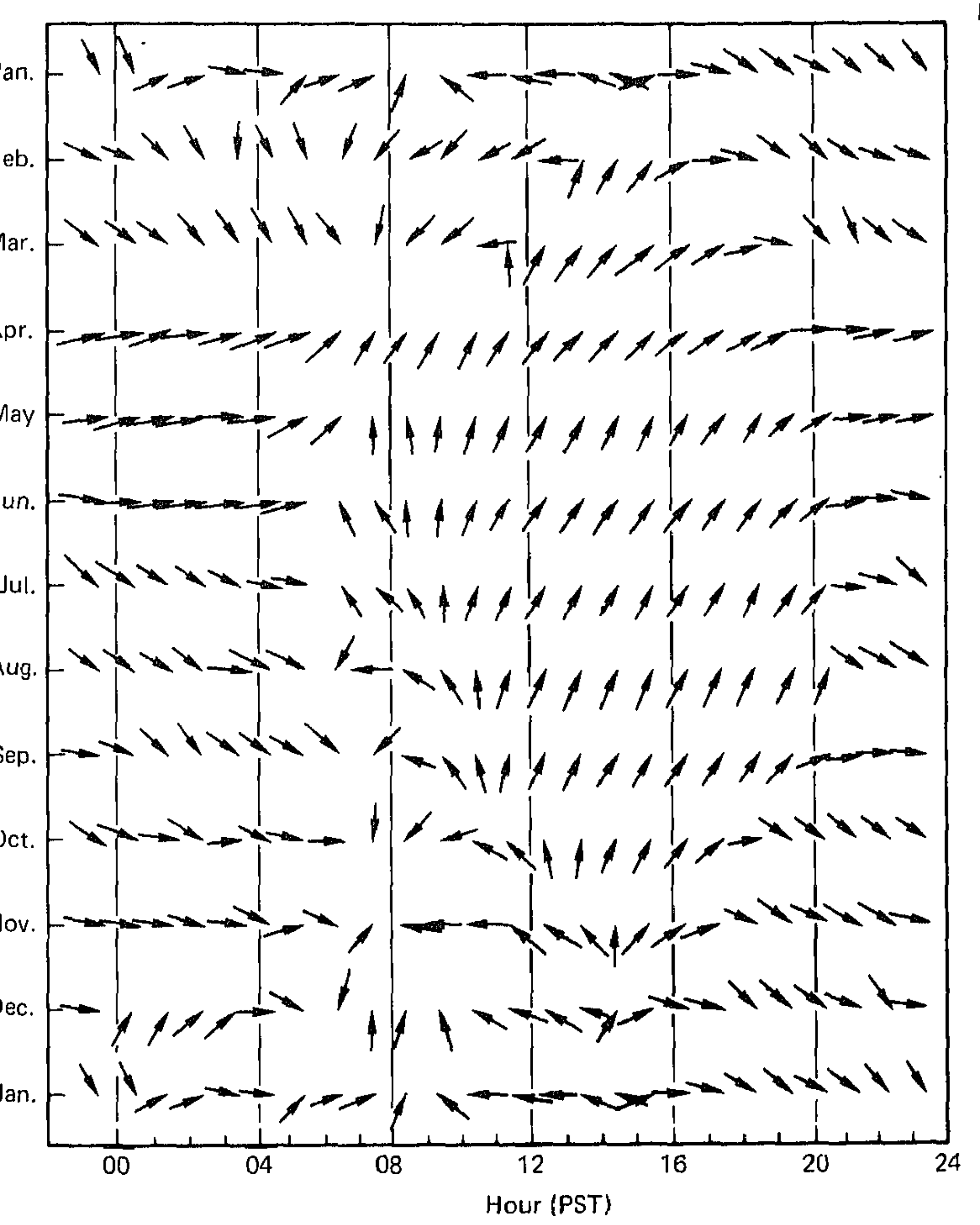


G. D-1(b). Monthly diurnal mean surface winds at Frenchman Flat, SYSTRAC Station 15 (Well 5B), for period January 197
bruary 1978. Based on 10-second wind observations at predominantly 15-minute sampling intervals (extended exceptions are 5-m

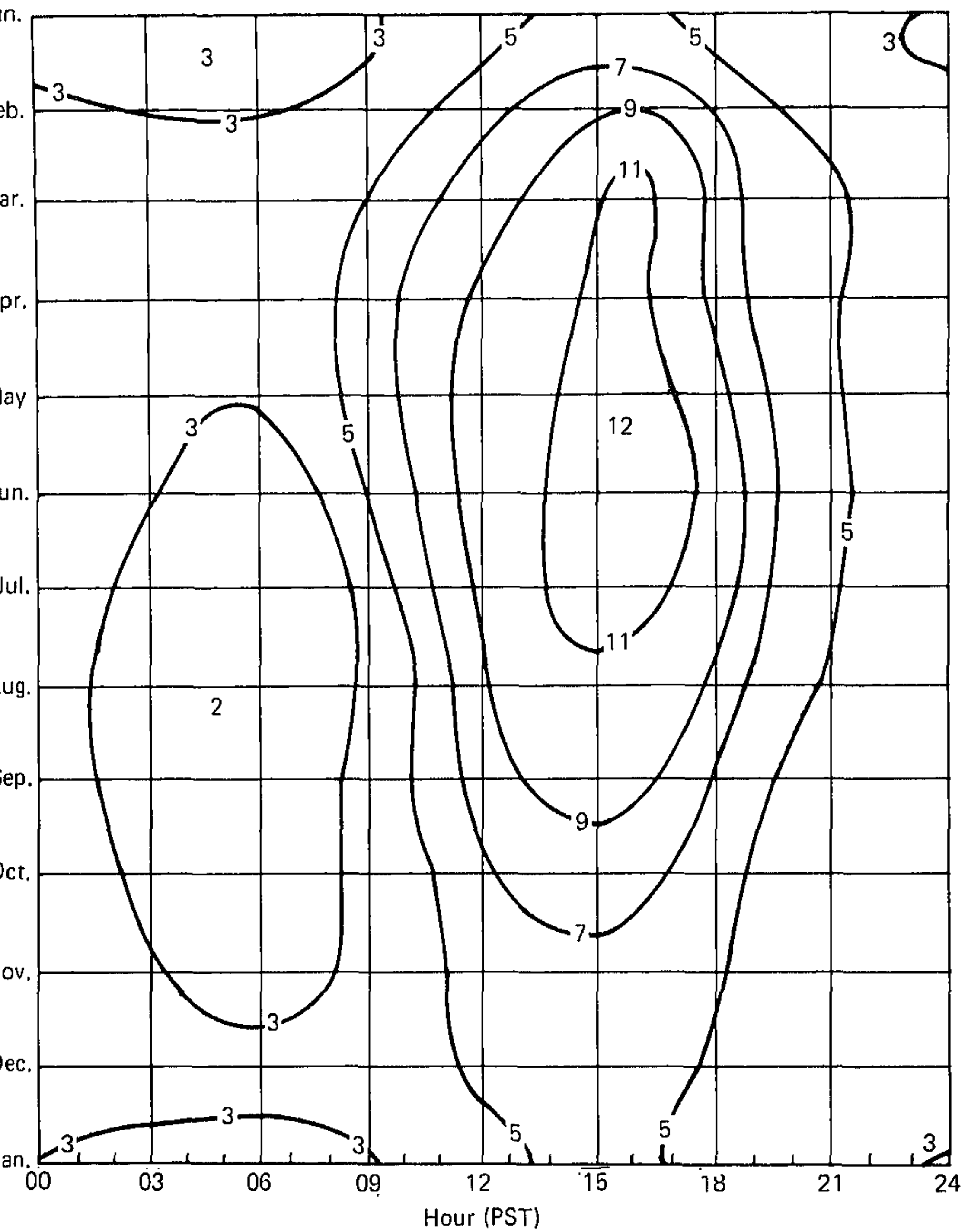
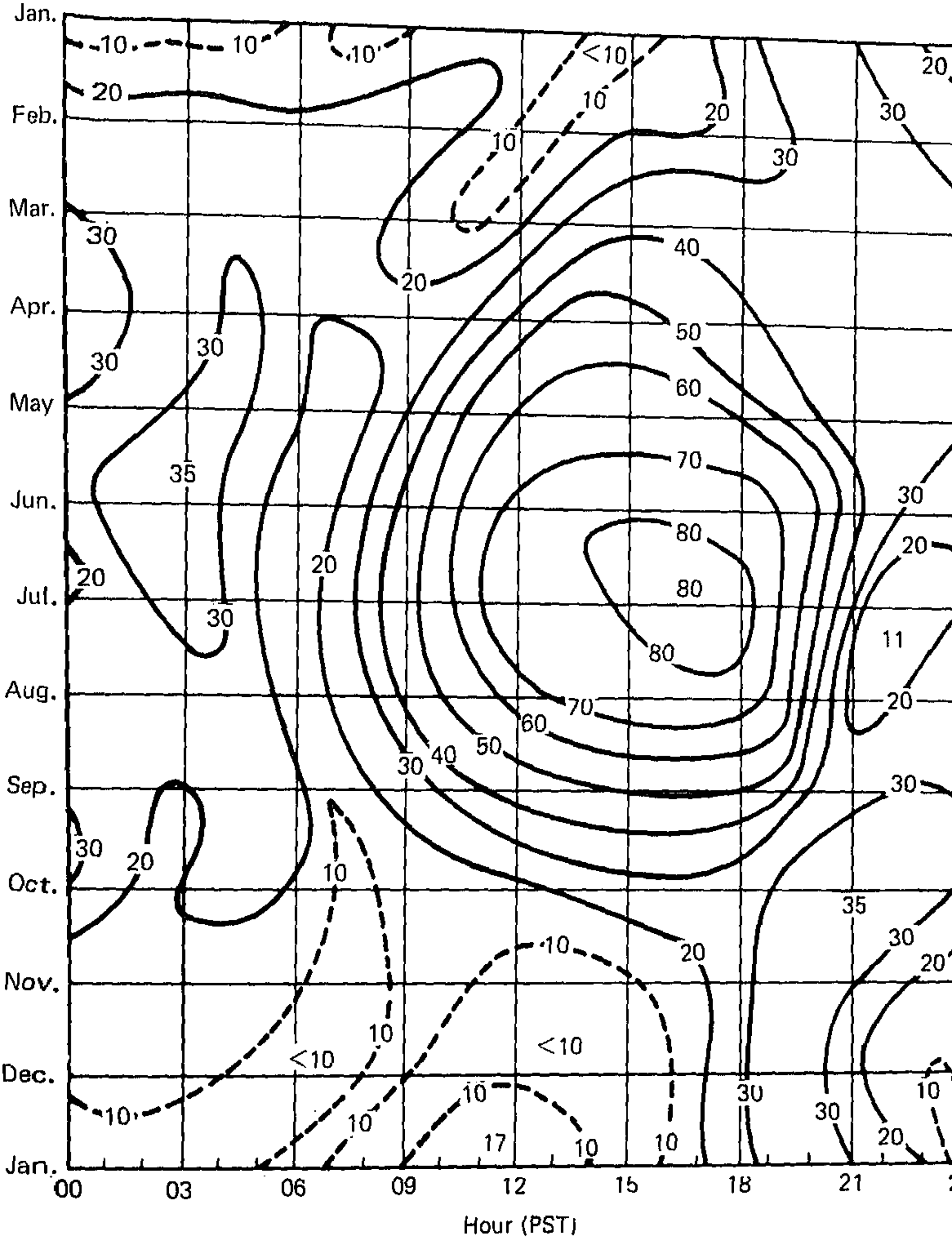


FIG. D-2. Monthly average wind speed (in knots) as a function of time of day (Station 15, Well 5B).



-3. Monthly constancy of the wind (expressed as percentage ratio of mean vector wind speed to mean scalar speed) as a functio
day (Station 15, Well 5B).

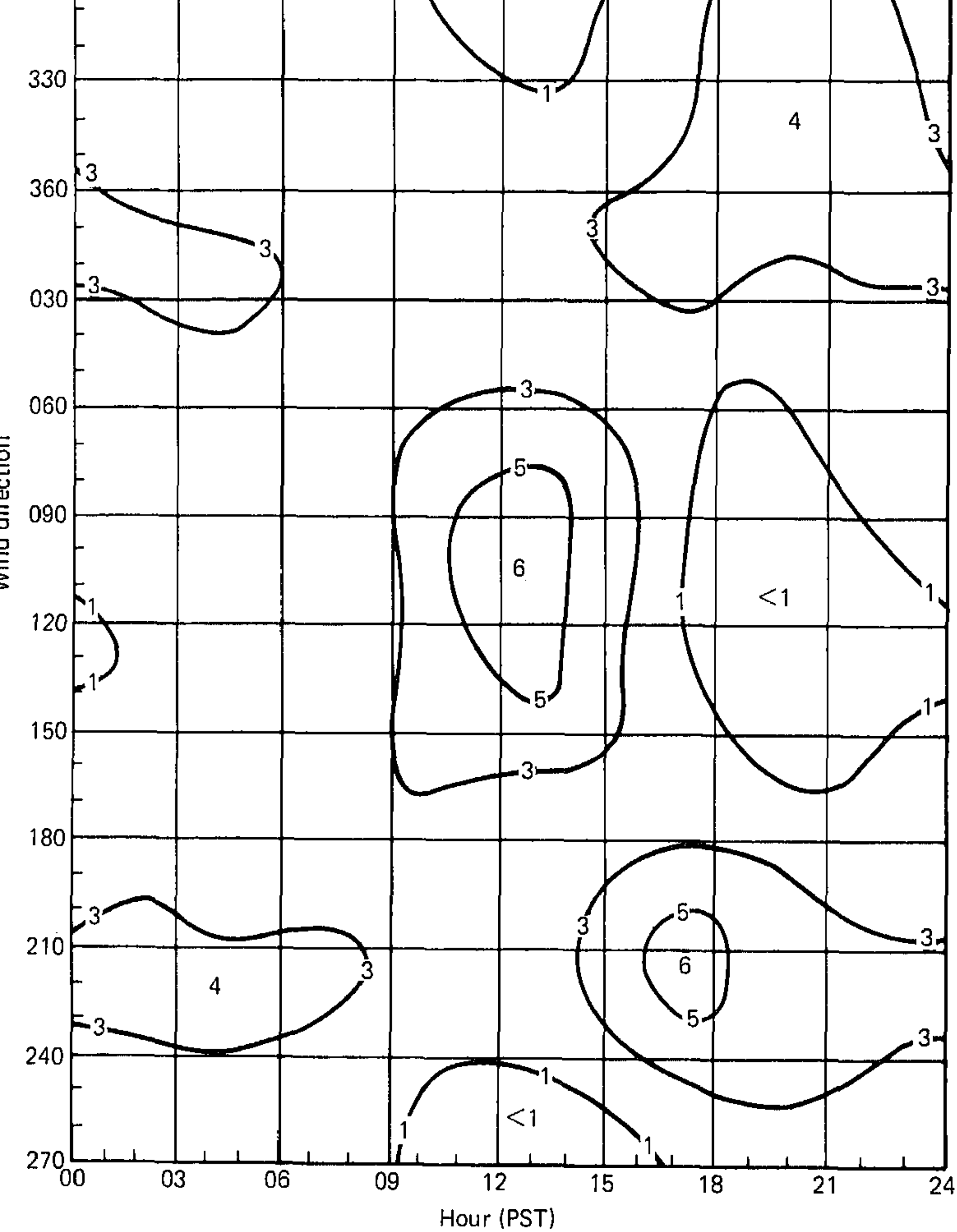
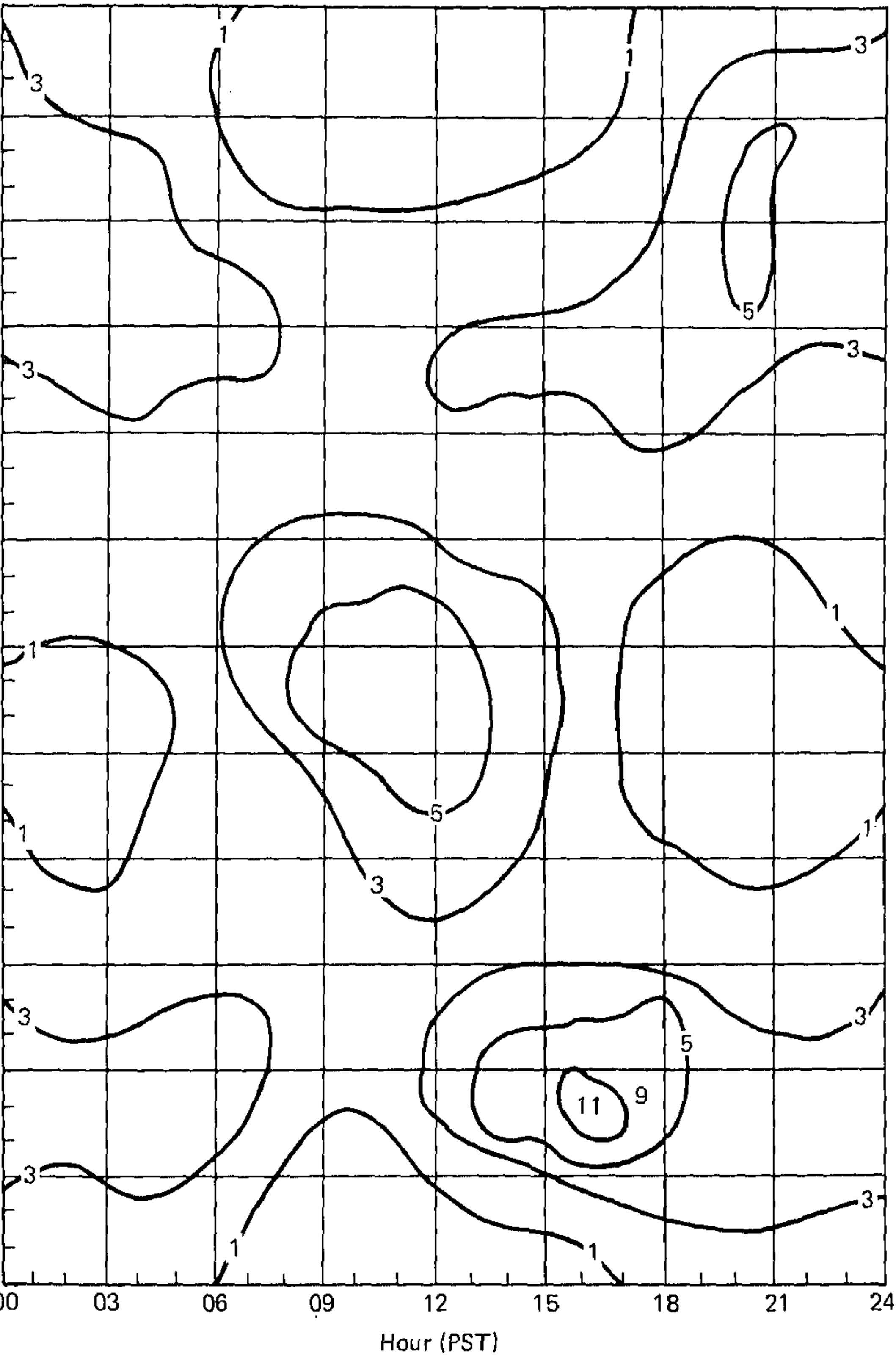


FIG. D-4. Wind direction frequency (%) for 10° increments of direction for month of January (Station 15, Well 5B).



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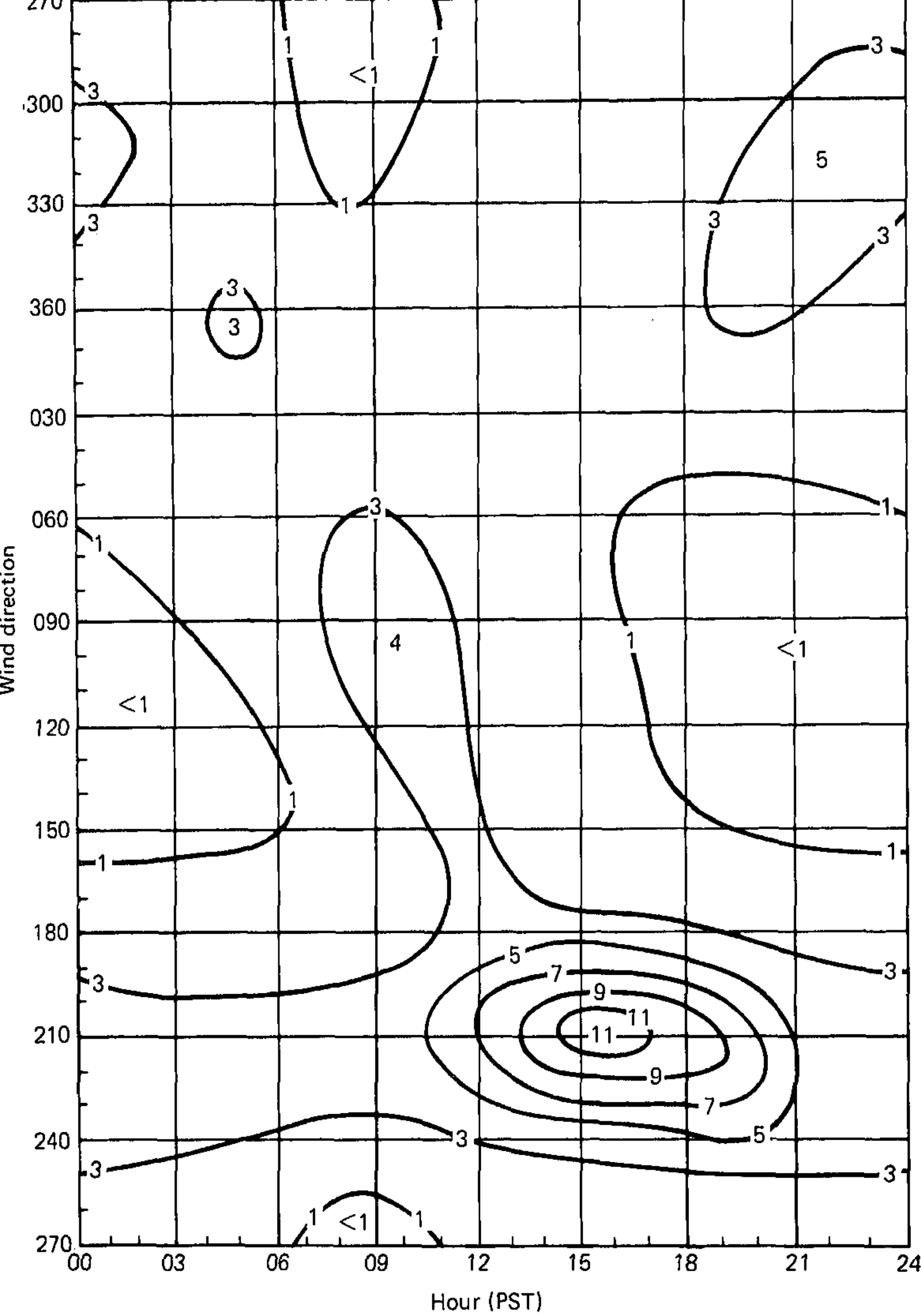
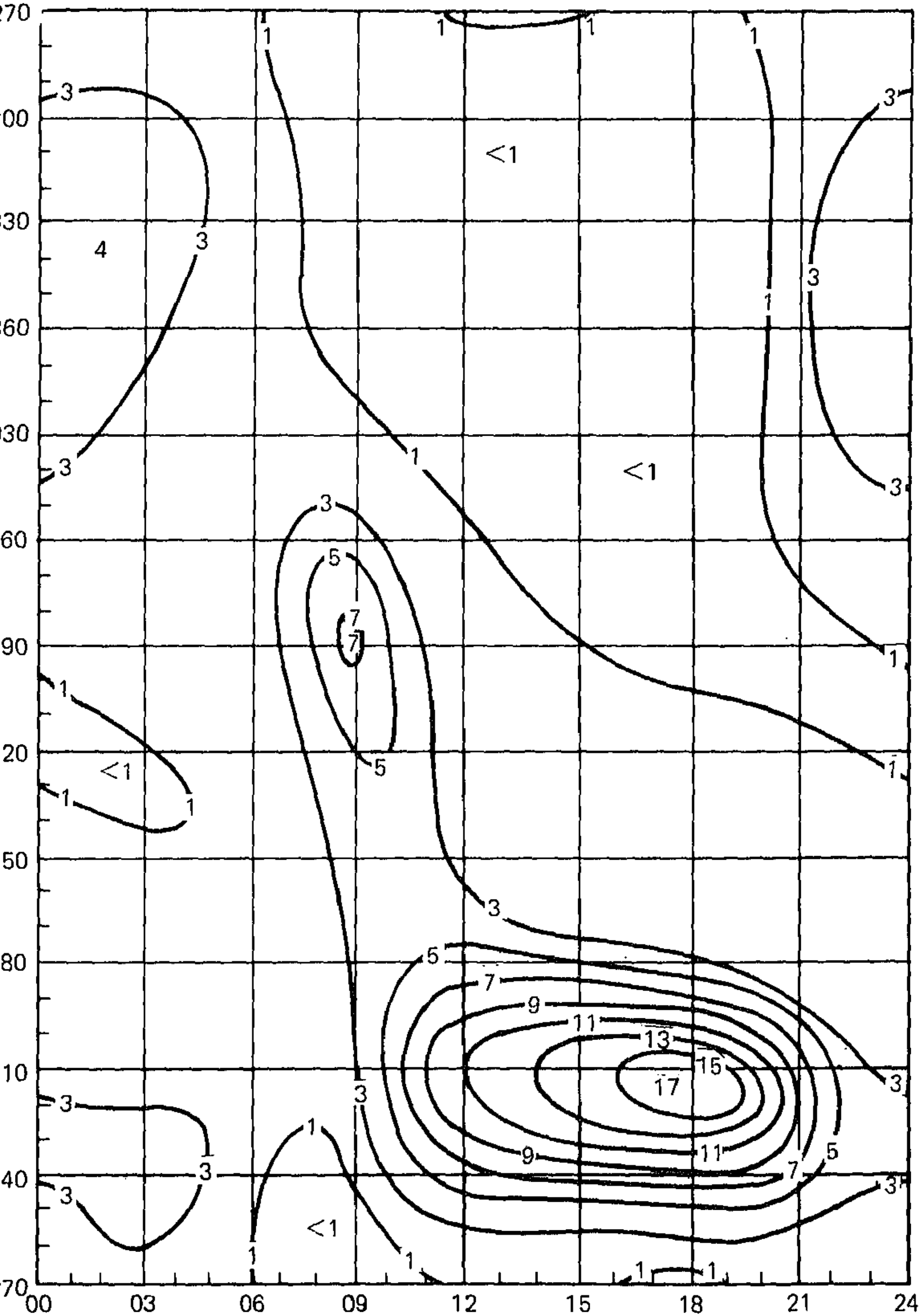


FIG. D-6. Wind direction frequency (%) for 10° increments of direction for month of April (Station 15, Well 5B).



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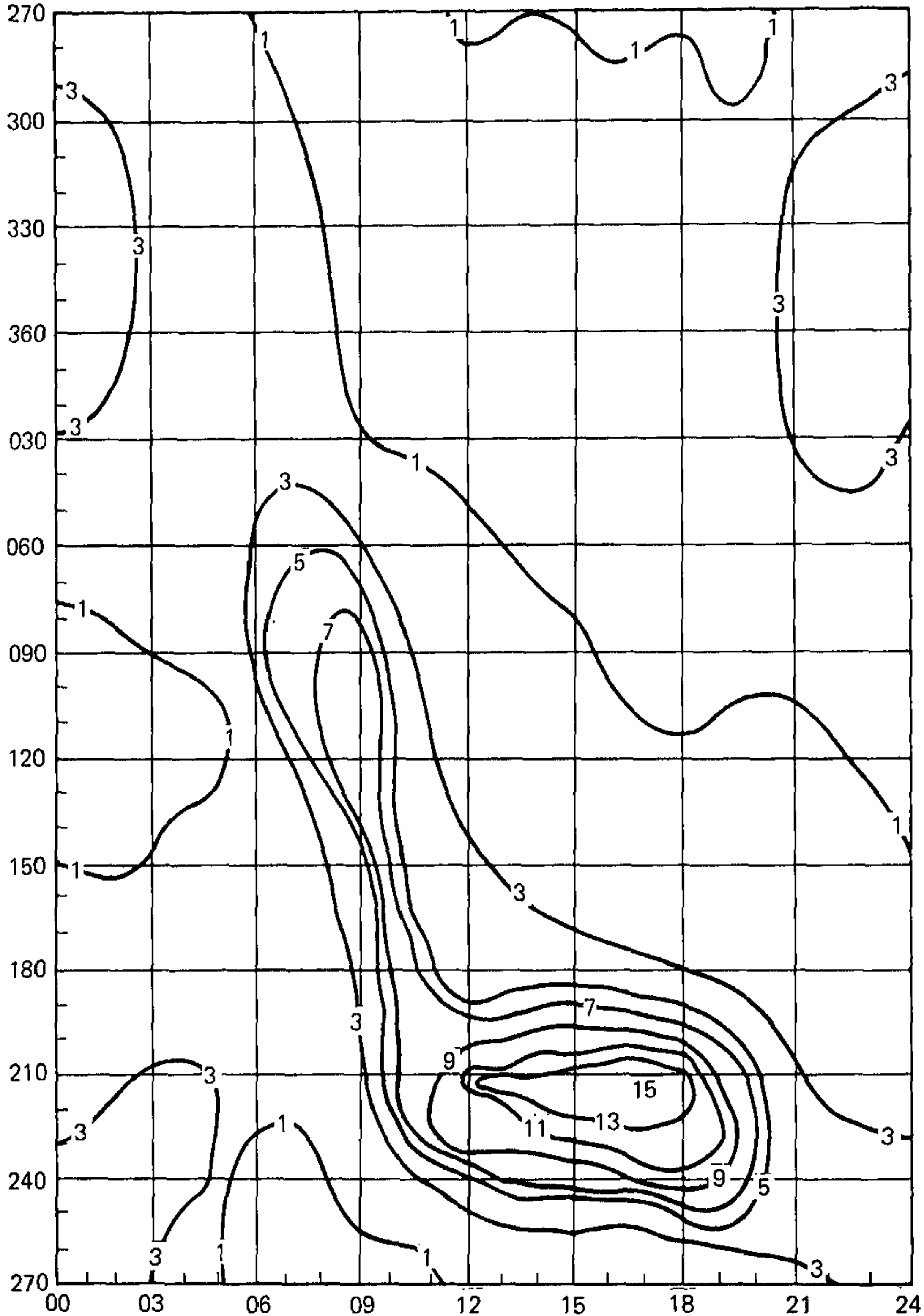

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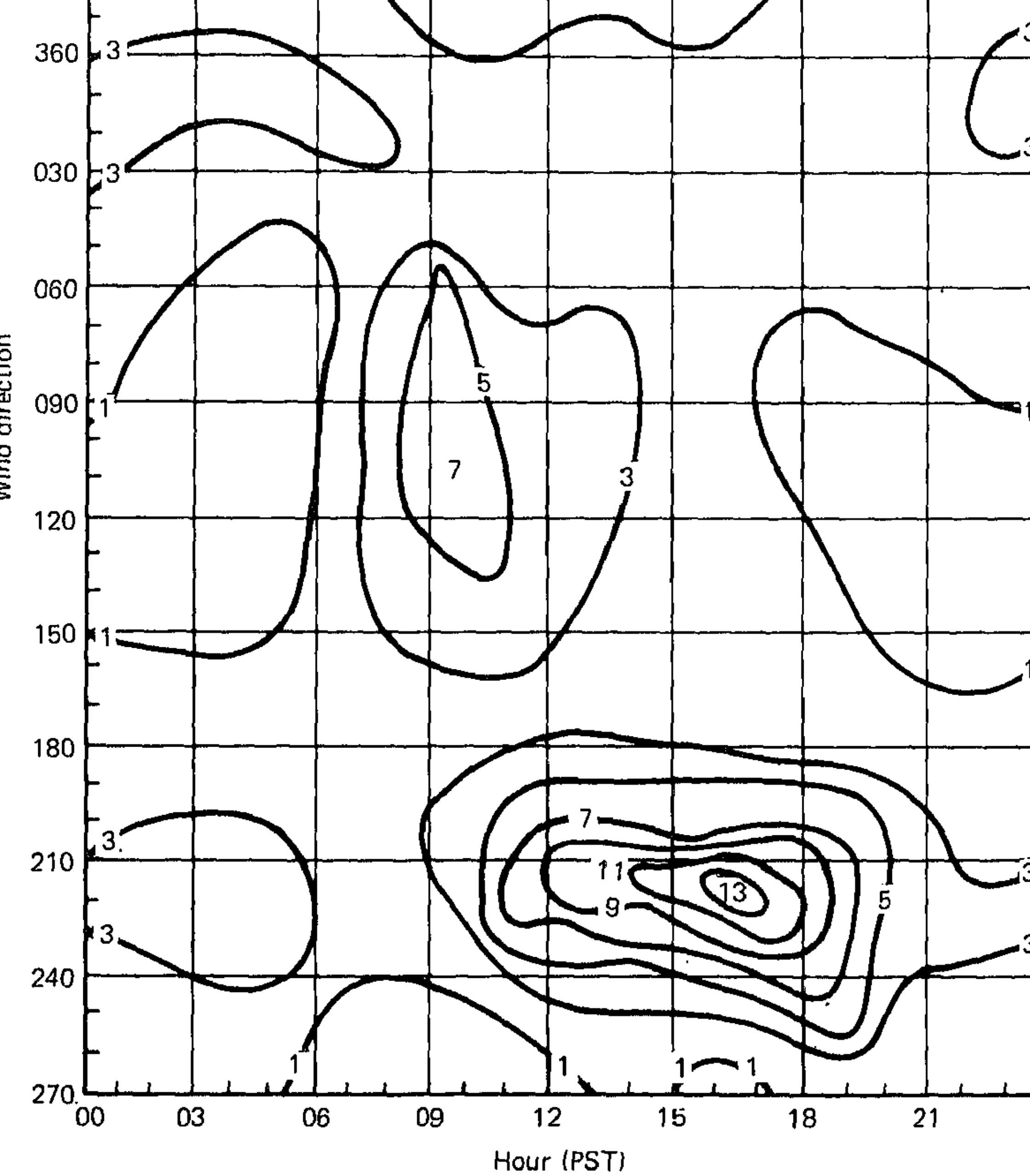
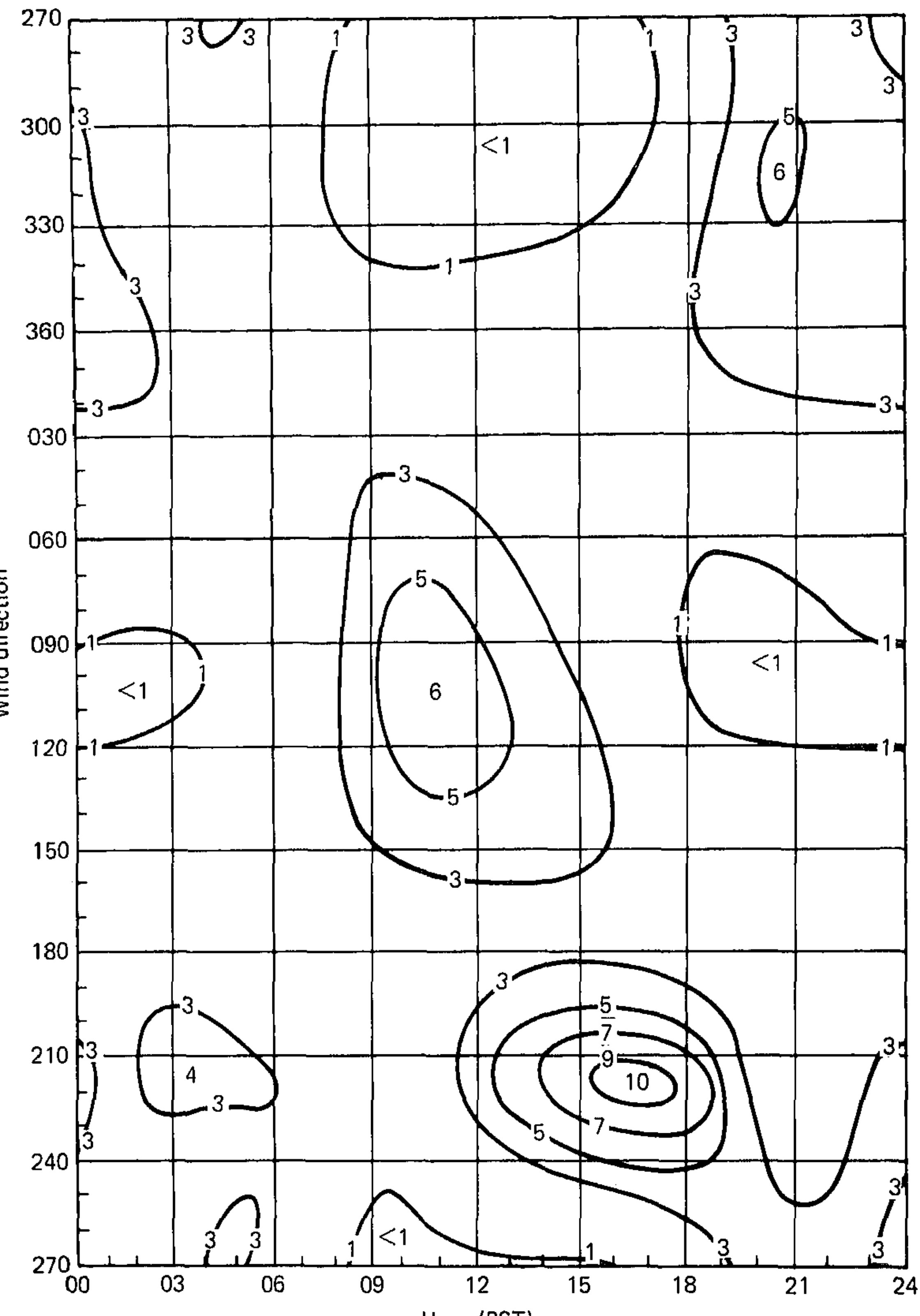


G. D-9. Wind direction frequency (%) for 10° increments of direction for month of September (1970-1978) (Station 15, V



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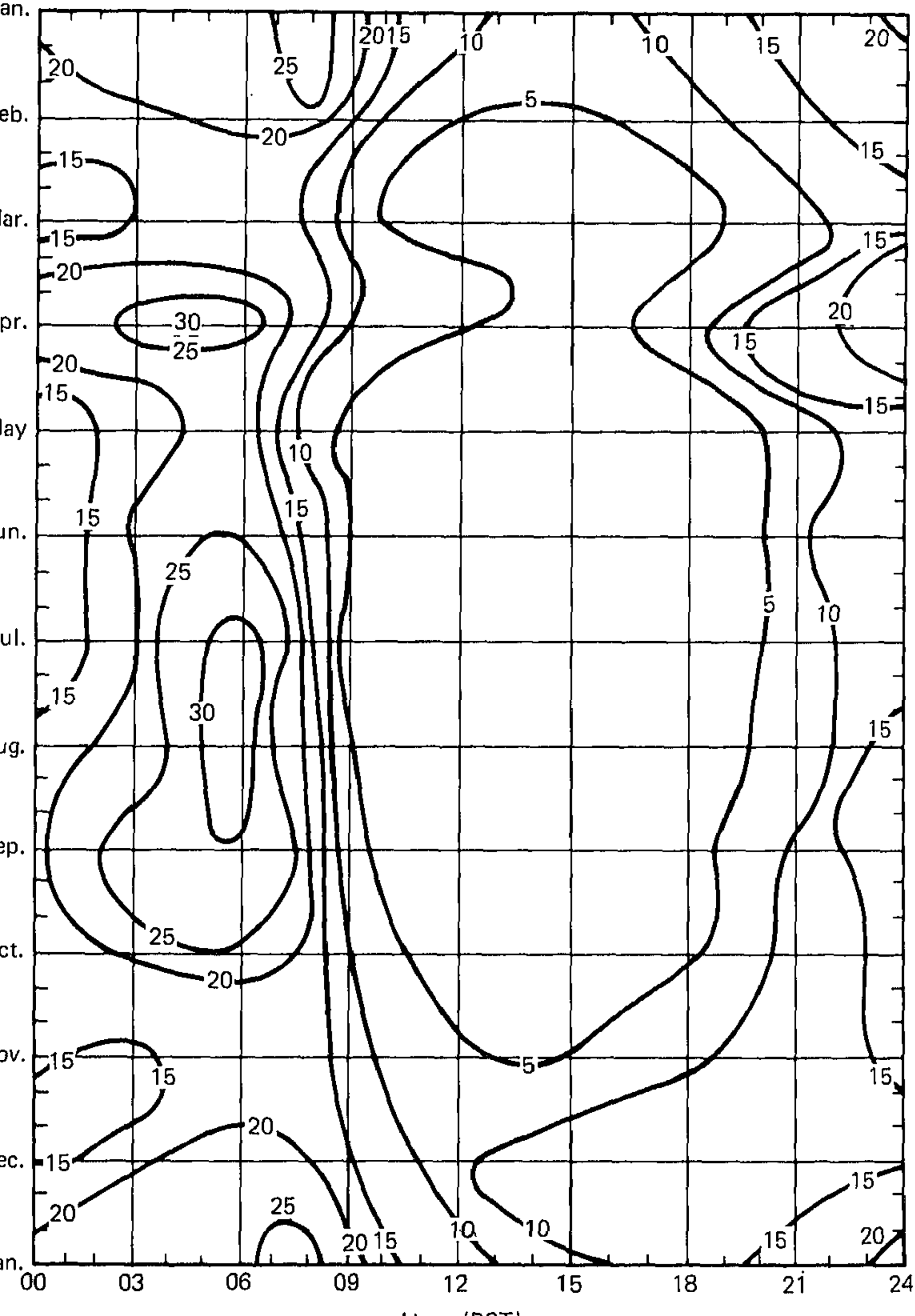

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by W. Stein

Spilling 1000 m^3 of LNG on a water surface may result in complete vaporization occurring in
ter of minutes. Two thermal hazards may occur from the LNG vapor: (1) the vapor may be ignited an
busted before it has a chance to disperse, in which case a fireball may occur with strong thermal ra
resulting; (2) the vapor may not be ignited immediately but instead may disperse and drift downwin
combustion occurring at any time before the cloud concentration falls below flammability limits.

Calculations based on Hardee's model[1] for maximum thermal radiation resulting from a fire
given in Fig. E-1. For this case the vapor has not been allowed to disperse and the location of the fireb
the spill site. From Fig. E-1, a thermal flux of 1 kW/m^2 (equivalent to solar radiation) is attained at a d
of 8600 m from the center of the fireball.

For case 2 involving combustion of the LNG cloud after it has dispersed downwind (see Refs
3), Fig. E-2 gives values of total distance, d_T, from the spill site out to a point where the thermal flux
to the solar thermal radiation level of 1 kW/m^2 as a function of time, t, and also as a function of dist
cloud travel, x.

Comparing Figs. E-1 and E-2, one observes that Fig. E-1, fireball radiation, represents the
thermal radiation hazard.

Based on the fireball model of case 1, the list in Table E-1 shows the distance, d, from the spil
which various thermal effects occur.

References

1. H. C. Hardee, Sandia Laboratories, Albuquerque, N. Mex., SAND-77-0602T (Aug. 1977).
2. H. R. Wesson, J. R. Welker, and L. E. Brown, "Control LNG-Spill Fires," *Hydrocarbon Proc*
   pp. 61-64 (Dec. 1972).
3. W. G. May and W. McQueen, "Radiation from Large Liquefied Natural Gas Fires," *Combustion*
   and Technology 7, 51-56 (1973).

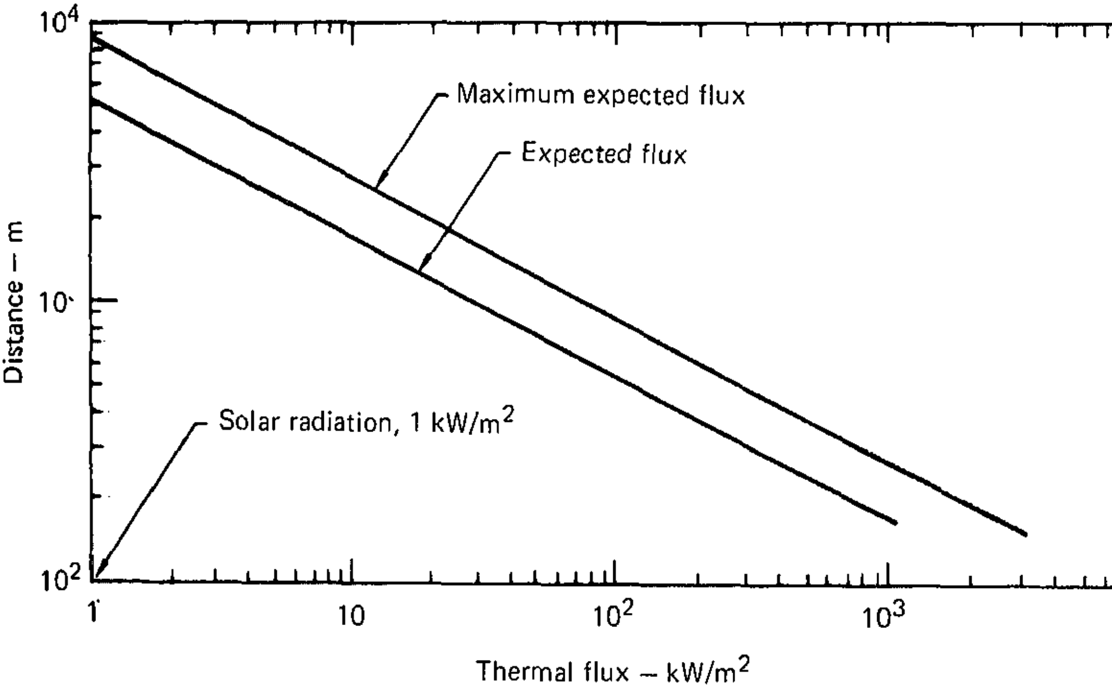
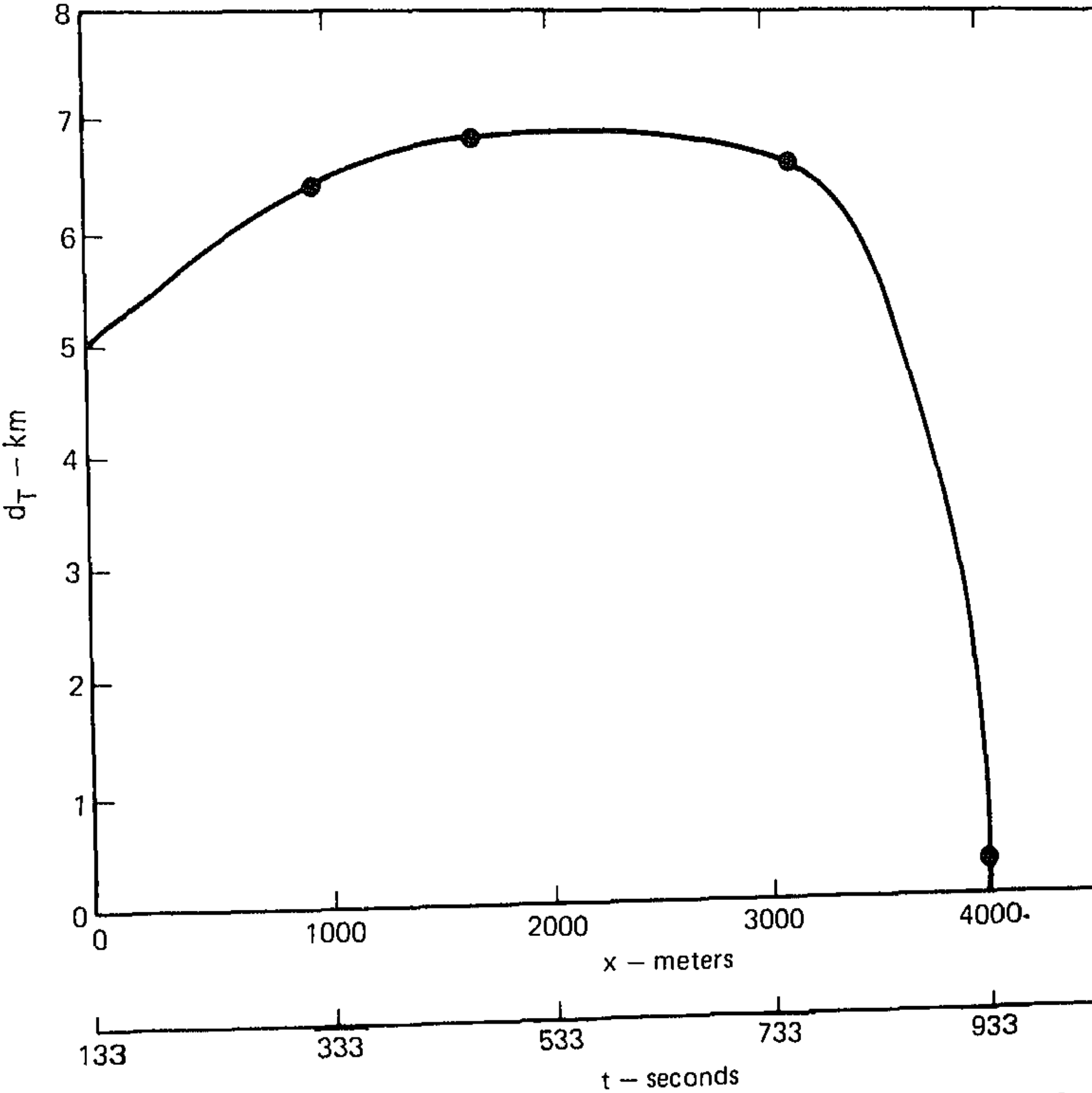


**FIG. E-1. Calculated thermal flux from fireball resulting from combustion of vapor cloud from 1000-m^3 LNG spill, as a function
rom the fireball.**

calculation of FIG. E-1.

Distance (m)	Flux (kW/m^2)	Damage produced
1950	20	Third degree burns on bare skin
1950	20	Combustion of bare wood
4300	4	Second degree burns on bare skin
8600	1	None (radiation equivalent to sunshine,



d_T = total distance from spill center to thermal radiation of 1 kW/m^2.

x = downwind travel of center of cloud from spill site.

t = time after initial spilling that cloud is combusted.

... from spill center of $1000\text{-}m^3$ LNG spill to thermal radiation level of 1 kW/m^2 (equivalent

APPENDIX F. APPROVAL MEMORANDUMS

Department of Energy
Nevada Operations Office
P.O. Box 14100
Las Vegas, NV 89114

MAR 6 1978

Dr. Richard L. Wagner, Jr.
Associate Director for Nuclear Test
Lawrence Livermore Laboratory
P. O. Box 808
Livermore, CA 94550

Dear Dr. Wagner:

You have approval to consider the Nevada Test Site (NTS) as a loca
for your liquified natural gas (LNG) spill facility as addressed i
your letter of January 9, 1978. However, approval of this project
will depend upon evaluation of your detailed proposals.

It appears that the Environmental Impact Statement for the NTS
adequately covers the proposed LNG experiments. However, appropri
attention shall have to be given to NTSO-SOP Chapter 6003, "Preser
tion of Antiquities and Historic Sites," prior to committing an ar
for the LNG experiment facility. Also, it is suggested that you
consider Jack Reed's (Sandia Laboratories) participation relative
blast and ducting effects.

Sincerely,

Mahlon E. Gates
Manager

cc: J. R. Gilpin, Dir., P&B
S. R. Elliott, Dir., OSH

Department of Energy
Nevada Operations Office
P.O. Box 14100
Las Vegas, NV 89114

August 2, 1978

Dr. R. L. Wagner
Test Director
University of California
Lawrence Livermore Laboratory
P. O. Box 808
Livermore, CA 94550

Dear Dr. Wagner:

APPROVAL TO CONDUCT LIQUID NATURAL GAS (LNG) SPILL EFFECTS TESTS AT THE NTS

A review of your proposal to conduct LNG Spill Effects Tests in the Frenchman Flat area of the NTS has been completed. Subject to the following conditions, approval of your request is hereby granted.

1. <u>Environmental Aspects</u>

The present final Environmental Impact Statement for the NTS addre high explosive tests of a chemical nature. We would expect, based our discussions with LLL staff to date, that the current EIS will suffice. Studies, however, of the effects of LNG on the environme during the smaller scaling experiments will be necessary in order confirm this belief. It is understood that public perception of L tests could exert pressures toward the preparation of an additiona assessment or statement for the larger tests. If it is not possib for you to perform these studies, funds should be provided to NV t perform them utilizing other contractors. We also request that yo prepare operational procedures which will protect the endangered plant species in Frenchman Flat, and otherwise minimize adverse environmental effects.

As a part of standard operating procedures at the test site, NV wi initiate an investigation of possible archaeological and historic cultural sites prior to any construction activities. If any such sites are found, NV will coordinate with the State of Nevada's Historic Preservation Officer as to their proper disposition.

2. Resuspension of Radioactive Particles

Due to the potential for resuspension and subsequent transport of radioactive material off the NTS during these tests, environmental monitoring will be required to document any release A release would require dose computation offsite and effluent reports.

3. Safety Plans

A safety plan must be submitted and approved by NV prior to the commencement of testing. This plan should emphasize safety and health aspects in relation to facility and equipment sitings, LNG aerial and ground surface monitoring grids, safety equipment, and medical and fire fighting support.

4. Public Affairs Plan

NV will issue an LNG Public Affairs Plan which will be adhered to by all program participants.

5. Construction Operations

All construction operations for the LNG Spill Tests will be performed, according to present NTSSOP's (6001), by DOE contracto at the direction of NV (NTSS).

6. Coordination

Coordination for area use permits should be effected within the DOE Operations Coordination Center - CP-1, Nevada Test Site. Experiments will be coordinated and reviewed by NV on an individu basis.

7.. Identification Badges

All visit requests and photographic permits should be submitted i writing, to the Director, Division of Safeguards and Security, ar received by NV, seven days in advance of the visit.

8. Passes for Access and Egress of Equipment

All vehicles and equipment with a list of contents must be submit to the Director, Property Management Division seven days in advar of delivery to arrange appropriate passes.

9. Transportation

The transportation of the Liquified Natural Gas must be accompli in accordance with the U. S. Department of Transportation and al other state and local government regulations. Additionally, the carrier used must have the authority to transport the substance.

10. Ability to Terminate the Program

NV will reserve the right to terminate the program at any time i is judged that its continuation will detrimentally affect other operations or facilities.

By copy of this letter, NV offices, agencies and contractors are to support the approved program. If you have any questions or require assistance in interpreting the aforementioned contingencies, please contact Wendy Arevalo, Plans and Budget Division - 598-3171.

Sincerely,

Mahlon E. Gates

Mahlon E. Gates
Manager

PBD:WRA-1443

cc: L. Crooks, LLL, Mercury, NV
T. T. Scolman, LASL, Los Alamos, NM
J. W. LaComb, FC/DNA, Mercury, NV
H. Runnels, REECo, Mercury, NV
B. C. Moore, Dir., NTSSO
H. E. Viney, SL, Albuq., NM
H. F. Mueller, NOAA/WSNSO, Las Vegas, NV
C. J. Smits, Dir., CMD
T. H. Blankenship, Dir., S&SECD

REPORT N

Validity of Desert Site Scale Effects Experiments

J. H. Shinn

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract W-7405-Eng-48

Lawrence Livermore Laboratory
Livermore, California 94550

REPORT N

TABLE OF CONTENTS

SUMMARY

A number of criteria are discussed to show that by the proper cho of atmospheric conditions and scaling criteria, most cases of atmosphe dispersion of LNG at a shoreline site can be simulated in a desert environment with an extensive spill pond. The criteria discussed are windspeed, lapse rate, atmospheric stability, heat flux, depth of the mixing zone, humidity, fetch, persistence, and turbulence scales. Cur studies to characterize Frenchman Flats are mentioned.

The objective of this report is to show that one can simulate in a desert environment the atmospheric dispersion of LNG at a shoreline site, through proper choice of atmospheric conditions and scaling crit

The assumption is made here that the purpose of a spill/simulatic is to determine how the dispersion of LNG differs from the classically defined dispersion of atmospheric tracer gases; it is not to simulate all possible problems of shoreline spills. Some particular flow probl specific to shoreline sites, such as the effects of sea breeze/land breeze circulations and terrain effects, are not being considered for simulation simply because they are too complex at this stage of resear In fact, that such effects will not differ from classical effects may determined during simulations of near-field LNG dispersion under simpl flow conditions.

It is also assumed that there are no operational restrictions on conducting experiments in the desert, so that, for example, experiment might be conducted at night in order to meet the several criteria that duplicate maritime conditions.

Discussion of Criteria

1. Windspeed frequency distributions show that scaling of the atmospheric surface boundary layer (similarity theory) will be possibl for any desired speed above 1.5 m/s. Below that speed, wind directior do not persist well enough ("light and variable" conditions) for controlled experiments. At the proposed Frenchman Flat (FF) site, a period of light and variable winds commonly exists between midnight ar sunrise in Summer and Fall.

2. The vertical temperature gradient (lapse rate) in the desert obtains the whole range from inversion to diabatic conditions. At FF the strongest diabatic lapse rates (Summer afternoons) are associated with strong winds, so that this combination allows a large range of mixes of forced and free convection regimes over the stability range from neutral to unstable. Only the rare maritime condition of extreme cold air flowing over warm water may be difficult to simulate in the diabatic case. Temperature inversions both near the ground in morning or elevated in late afternoon and evening give ample cases for simulating maritime mixing depths.

3. The atmospheric stability conditions for sites of proposed LN terminals in New Jersey, Louisiana, and California typically show neut stability about 50% of the time and either slight unstability or sligh stability 20-25% of the time. These same conditions are found at dese

sites such as Frenchman Flats. Gifford[1] points out that "c stratification over water is controlled not only by the hea over land, but also depends on the water-vapor flux". This be simulated in the desert, providing the experiments take within the humidity boundary layer over sufficiently extens A spill site 300 m from the leading edge of a deep pond and shallow water surfaces extending more than 2 km in the down are the minimum design requirements (such as proposed at Fl

There are several alternative stability criteria in co diffusion predictions. The preferred, dynamically-correct Monin-Obukhov parameter, but more easily measured and direc are the Richardson Number and "sigma theta" (the standard c wind direction azimuth angle given in radians). An overly- practical classification system commonly called the Pasquil curves is to be avoided. Lyons[2] states that "the main dif applying the P-G stability curves is that the criteria ofte select the appropriate class may only truly apply to the lo that research was performed", which usually "bears little the lake-shore environment." Lyons also points out that th of "conduction inversions" and other cases observed at Broo Laboratory where the experimentally observed dispersion was a super-stability. These cases are not well studied and w simulated in the desert on the basis of what is now known.

4. <u>The heat flux from water to air</u> depends upon a bu coefficient (D). The heat transfer process to cold natura a slightly different process if the cold pool of gas is la suppress turbulence. Nevertheless, comparison of D values for discussion of whether similarity exists between heat ex shallow ponds in the desert and heat exchange from offshore *et al*[3] determined from measurements on a meteorological bu were 1.2×10^{-3} with an uncertainty of 20%. Emmanuel[4] foun lake D values were 1.2×10^{-3} and by reviewing other work all reported D values could be reconciled within an uncerta Hicks[5] determined that the dependency of D on wind speed r only exists if the water is either extremely colder than t stable) or extremely warmer than the air. The implication and swells have little effect on the bulk heat transfer an ponds in the desert are sufficient simulators for convecti in offshore sites. However, it should also be realized th factor in determining the average temperature of the natur will be the rate of adiabatic entrainment of ambient air i gas rather than convective heating. A modulus (BFM) was d Meroney *et al*[6] as the ratio of the time the cold plume is surface to the time lag for heat transfer to occur. The B

than one, which means that (in the vapor phase at least) convective he transfer is not as important as adiabatic entrainment.

5. The depth of the mixing zone in the desert is determined by t height of the inversion layer, which grows during the day as a result turbulent entrainment, from a minimum height (less than 100 m) near sunrise to reach a maximum about sunset which often exceeds 1 km. The frequency of occurrence of certain height classes and their joint corr tion to wind speeds and stability classes has not been studied, even f such desert sites as Frenchman Flats, but recent theoretical treatment (Zeman and Tennekes, 1976)[7] have developed a better understanding of mixing depth dynamics. It is quite possible to monitor the depth of t mixing zone to determine these statistics to be used as planning aids, in the meantime, it suffices to point out that during operations for L spills, monitoring would be a method for selecting spill conditions wh closely simulate maritime conditions.

6. The humidity in the ambient air at proposed LNG terminals is typically 65% in daytime and 80% at nighttime, being slightly higher o the Gulf Coast than in California and New Jersey. Although absolute humidity is lower in the desert, it is not unusual to have relative humidities 50-80% at night. Also, a water vapor boundary layer will develop over an horizontally extensive spill pond, so that LNG will be spilled in a humid envelope similar to what exists in maritime conditi The "working depth" of this water vapor boundary layer will typically a few meters at a distance 300 m from the leading edge of a spill pond and will continue to grow as $x^{4/5}$ in the downwind direction for a distance more than 2 km for the site proposed at FF. Obviously, it will be possible to simulate saturated conditions or fog in the desert.

7. The upwind distance (fetch) to a meteorological discontinuity has to be maximized so that horizontal gradients of wind speed, temper and humidity are vanishingly small and so that turbulence will not be artificially generated in the region downwind where the spilled LNG gr itational spreading, boiloff, and dispersion are occurring. In past L spill experiments, these conditions have not been adequately met.

The need for a well-developed heat and humidity boundary layer wa discussed previously as was the requirement for a minimum 300 m fetch the spill site and downwind range of 2 km. In addition, turbulent wak will persist for distances of 10 L downstream of buildings, tanks, fences, towers, dikes, etc., where L is a characteristic dimension (L perhaps best estimated by the square root of the object silhouette are This requirement can be obtained by eliminating or burying unnecessary obstacles, streamlining the few necessary dikes, and moving supporting structures outside the study area. At FF, the extensive playa provide

8. The persistence of windspeed and direction for a peri
10 minutes is necessary to obtain a meteorological "steady sta
there are two time scales of importance. The first is a short
which defines the limit of turbulent variance of properties su
temperature, and wind, or fluxes such as heat and momentum. T
scale varies directly with height above ground, inversely with
and increases by a factor of 3 from stable to unstable conditi
cally this time scale is less than 1 minute, but in order to e
the full spectrum of turbulence, an LNG spill must continue fo
greater than this time scale.

The second time scale extends for a minimum of 10 minutes
maximum of thirty minutes, by convention, and represents a per
which the micrometeorologist can expect scales of motion and h
to be relatively constant.

An LNG continuous spill simulation in the desert must be
during a period represented by these scales, both in order to
meaningful and to get results that correctly scale to maritime

9. Turbulence scales over the ocean have been examined b
Pond[8] and by SethuRaman *et al*[9] and, for example, the turbulenc
were found to scale in the same manner as over terrestrial sit
example, turbulence measurements in the desert, at White Sands
Range[10] and at Palmdale, California[11] demonstrated that the co
of desert environments produces no surprises in our similarity
As a result, there is similarity between maritime and desert s
the other hand, wind tunnel simulations usually have an entire
set of turbulence scales and frequencies relative to the chara
scales of mean flow.)

Studies to Characterize Frenchman Flats

The historical data for Frenchman Flats and for nearby si
Nevada Test Site are not complete enough for certain purposes.
data are being collected at five levels on a 62 m tower in ord
struct joint frequency distributions of the criteria described
prior to LNG spill operations. In addition, five portable sta
continuously measure wind speed and direction are being distri
surrounding air drainage basin to determine flow patterns.

Since there are some uncertainties about the heat exchang
above a shallow pond in the desert, a short-term study is bein
to determine the energy balance (due to turbidity - a high sol

at exchange coefficient, temperature (difference from air), and midity boundary layer using standard micrometeorological flux-adient techniques.

Later this year a study of the depth of the mixing zone over enchman Flats will be undertaken in order to develop a climatology d predictive technique for LNG spill operations.

References Cited

1. Gifford, F.A., Atmospheric Dispersion Models for Envi
Pollution Applications, Chapter 2, Lectures on Air Po
Environmental Impact Analyses, American Meteorologica
Boston, 1975.

2. Lyons, W.A., Turbulent Diffusion and Pollutant Transp
Shoreline Environments, Chapter 5, Lectures on Air Po
Environmental Impact Analyses, American Meteorologica
Boston, 1975.

3. Pond, S., G.T. Phelps, and J.E. Paquin, Measurement c
Fluxes of Momentum, Moisture, and Sensible Heat over
J. Atmospheric Sci., 28 (6) 901-917, 1971.

4. Emmanuel, C.B., Drag and Bulk Aerodynamic Coefficient
Water, Boundary Layer Meteorology, 8, 465-474, 1975.

5. Hicks, B.B., A Procedure for the Formulation of Bulk
Coefficients over Water, Boundary Layer Meteorology,

6. Meroney, R.N., J.E. Cermak, and D.E. Neff, Dispersion
LNG Spills - Simulation in a Meteorological Wind Tunn
Symposium on Atmospheric Turbulence, Diffusion, and A
Raleigh, N.C., October 19-27, 1976, pp 243-246, Prepr
American Meteorological Society, 1976.

7. Zeman, O. and H. Tennekes, Parameterization of the Tu
Budget at the Top of the Daytime Atmospheric Boundary
Atmospheric Sci., 34, 111-123, 1977.

8. Phelps, G.T. and S. Pond, Spectra of the Temperature
Fluctuations and of the Fluxes of Moisture and Sensit
the Marine Boundary Layer, J. Atmospheric Sci., 28, 9

9. SethuRaman, S., R.E. Meyers, and R.M. Brown, Ratio of
Eulerian Energy Dissipation Scales over Water During
Third Symposium on Atmospheric Turbulence, Diffusion
Raleigh, N.C., October 19-27, 1976, pp 264-268, Prepr
American Meteorological Society, 1976.

10. Monahan, H.H. and M. Armendari, Gust Factor Variation
and Atmospheric Stability, J. Geophys. Research, 76 (
1971.

11. Aldefang, S.I., Standard Deviation of Turbulence Velo
over Flat, Arid Terrain, J. Geophys. Research, 75 (3

REPORT O

Experimental Strategy Considerations for LNG Field Experimentation

F. R. Zaloudek
W. C. Cliff
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R. A. McCann
T. E. Donovan
R. J. Hall

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352
Operated by Battelle Memorial Institute

REPORT 0

TABLE OF CONTENTS

TABLES

1.0 SUMMARY

This report provices the results of a study undertaken to develop
nsights into the characteristics of various experimental strategies a
dvantages as applied to the planned field experiments portion of the
afety and Environmental Control R&D Program. Advantages can only be
ined relative to a particular set of constraints, e.g., program objec
esources available, process characteristics and process understanding
he absence of definitive information, assumptions were made about con
ased on these assumptions, experimental strategies and experimental r
atrices were analyzed. Confirmation of the assumptions was beyond th
f the study.

Experimental strategies and run matrices were developed for the f
NG spill phenomena: (1) vapor generation and dispersion, (2) vapor c
and possible explosion) and (3) pool fire. Both the classical approa
he statistical approach were considered. The classical approach invo
one-variable-at-a-time" experimentation. It is technically sound but
equire a very large number of experiments. The statistical approach
haracterized by experimentation in which several variables are simult
tudied by varying them in a predetermined pattern. It is particularl
ive in identifying and defining the influence and interaction of many
ithout excessive experimentation. Through actual or effective replic
nd randomization, the effects of experimental error can be defined an
inimized. This approach can adequately cope with situations where th
re important uncontrollable or marginally controllable influences in
xperiment. The statistical type strategy was selected as best suited
he LNG field experiments program.

A preliminary set of experimental matrices relating the required
nd the respective magnitude of important parameters for each test is
iven. Development of the matrices involved the following steps: (a)
ification of parameters involved in each of the three LNG spill pheno
isted above, (b) assessment of the importance of each parameter, (c)
ation or selection of the range of values for each parameter assessed

t of the experimental matrix of run number and parameter size such that results of these tests will separate, and show, the behavior of the im iables. The assumptions and rationale used in each step are presented.

Since the optimum experimental strategy and matrix are strongly deper the unconfirmed assumptions on program constraints, the results of this dy should be viewed only as guidance and a starting point for developir experimental strategy for the LNG field experiments program.

2.0 INTRODUCTION

The Department of Energy is conducting a combined analytical- study to improve the technical bases for regulatory decision makin to LNG safety. The behavior of a large release of LNG is currentl technical issue. The issue revolves around points such as:

- The distance from an LNG spill at which the vapor cloud is ig and will propagate back to the source.
- The maximum distance from an LNG spill at which a thermal or pressure hazard can exist for various spill conditions.
- Whether an explosion can propagate in a vapor cloud and if so local surface temperatures and overpressures that could resul
- The total radiative power of a free-burning flame at location the radiation may be intercepted by people and structures.

Field experiments to study LNG release phenomena are planned as a effort to address this issue. Because of the size of LNG equipmen vessels, releases on the order of tens of thousands of cubic meter are theoretically possible.

This study was undertaken to provide initial insights to the tics, and advantages and disadvantages, of various experimental st application to the LNG field experiment program. In order to sele candidate experimental strategies, constraints on the program and effort must be identified or postulated. It was postulated that t constraints on the field experiments efforts would be set by the p objectives and resources (time, money, LNG) available for carrying experiments. (Although time and costs were not quantified in this their minimization was a guiding consideration in the analysis of strategies.) Given these constraints, a full scale field test pro ruled out as prohibitively expensive and a questionable use of key resource. Therefore, it was concluded that the main purpose of th experiment effort should be to support the analytical effort throu

modification and/or further development of existing methods or codes are needed, incidental guidance and support should be provided to the degree possible by phenomenological information obtained from laboratory experi- ments.) This verification testing will be characterized by the followin factors:

- The experiments will be relatively large (but smaller than full sca and expensive.
- There will be many independent variables.
- Large random and uncontrollable influences may be present.

Because of the possible presence of random and uncontrollable factors, t performance of several large "demonstration"-type tests can give only qualitative indicative information on the applicability of the analytic methods and codes. This is not consistent with the purpose of the progr and therefore this experimental strategy was not considered in the prese study.

This study specifically provides direction and procedures for deter the minimum number of experimental tests required to separate, and confi calculated behavior and effect of, important parameters associated with different potential LNG spill phenomena: (1) vapor generation and dispe (2) vapor cloud fire (and possible explosion) and (3) pool fire. Both t classical approach and the statistical approach are considered.

3.0 PARAMETERS INVOLVED

This section lists the parameters which it was felt could affect th
rious LNG spill phenomena. The following lists are not claimed to be
mplete but are rather lists generated over a short period of time with
e hope that the major parameters have been identified.

1 PARAMETERS ASSOCIATED WITH LNG VAPOR GENERATION AND DISPERSION

Spill Characteristics

- Volume
- Rate
- Spill shape, area
- Spill surface

Vapor Generation

- Air Pressure
- Spill Surfaces
- Thermophysical Properties (of, e.g. LNG, materials contacting spill)
- Ground Temperature
- Water Temperature
- LNG Composition
- Pool Depth
- Water Characteristics

Vapor Transport, Wind

- Wind Direction
- Wind Speed

Vapor Transport, Gravitational Spreading

- Topography
- Structures (constraints to the spreading)
- Source Elevation (above grade level)
- Spill Volume
- Water Pick-up
- LNG Composition

Vapor Dispersion, Atmospheric Turbulence

- Temperature Lapse Rate
- Temperature Difference (air, water)
- Temperature Difference (air, ground)
- Temperature Difference (ground, water)
- Air Pressure
- Vertical Wind Shear

Structures (Modification of flow field)
LNG Pool Temperature

Vapor Dispersion, Heat Addition to Vapor Cloud

Air Temperature
Water Temperature
Ground Temperature
Solar Radiation
Cloud Temperature
Relative Humidity

3.2 PARAMETERS ASSOCIATED WITH LNG VAPOR CLOUD FIRES

Initial Conditions

Size and Shape of Gas Cloud
Concentration of Gas Species
Cloud Temperature
Wind Shear
Turbulence (Atmospheric)
Other Meteorological Conditions
Ignition Source Type and Location
Topography
Structures
Water Vapor

Flame Propagation

Reaction Mechanisms
Chemical Kinetics
Thermodynamic, Transport and Thermophysical Properties
Optical Properties

3.3 PARAMETERS ASSOCIATED WITH LNG POOL FIRES

Initial Conditions

Pool Size
Pool Shape
LNG Composition
LNG Temperature
Wind Velocity
Turbulence (Atmospheric)
Other Meteorological Conditions
Topography and Structures
Spill Surface (Water, Land)

Fire Dynamics

Reaction Mechanics
Chemical Kinetics
Thermodynamic, Transport and Thermophysical Properties
Optical Properties

4.0 PARAMETERS TO BE VARIED IN FIELD EXPERIMENTS[a]

The following parameters were selected as potentially having firs order effects on the following LNG processes.

4.1 PARAMETERS TO BE VARIED FOR LNG VAPOR GENERATION AND DISPERSION T

Spill Volume
Spill Rate
Spill Surface (land, water, concrete)
Wind Speed
Richardson Number (atmospheric stability measure)
Surface Roughness (aerodynamic)
Heat Input to Cloud

4.2 PARAMETERS TO BE VARIED FOR LNG VAPOR CLOUD FIRE TESTS

Size and Shape of Gas Cloud
Concentration of Gas Species
Wind Speed
Surface Roughness
Ignition Source Location
Ignition Type
Water Vapor
Richardson Number (Atmospheric Stability Measure)

4.3 PARAMETERS TO BE VARIED FOR LNG POOL FIRE TESTS

Pool Size
Wind Speed
Surface Roughness
Spill Surface (Land, Water)
Richardson Number

(a) See Appendix A for the rationale used to select the parameters to varied in the LNG tests.

5.0 PARAMETER RANGE FOR FIELD EXPERIMENTS

The following provides the estimated range of those variables identif
otentially having a first order effect on the following LNG processes.

PARAMETER RANGE FOR LNG VAPOR GENERATION AND DISPERSION TESTS

Spill Volume[(a)]

Land: 4-20 m^3
Water: 100-1000 m^3

Spill Rate[(b)]

Land : 2-40 m^3/min
Water: 10-1000 m^3/min

Spill Surface: Soil; insulated concrete; water
Wind Speed: 0-9 m/s (0-20 mph) measured at 9.1 m (30 ft)[(b)]
Gradient Richardson Number (R_0): $-1.0 \leq R_0 \leq 0.2$[(b)]
Surface Roughness: 0.0001 m to 1.0 m[(c)]
Heat Input to Cloud (likely dominated by air temperature): to be det

PARAMETER RANGE FOR LNG VAPOR CLOUD FIRES TESTS

Size and Shape of Gas Cloud: that resulting from 100-1000 m^3 spills(
Concentration of Gas Species: to be determined
Wind Speed: 0-9 m/w (0-20 mph) measured at 9.1 m (30 ft)[(b)]
Gradient Richardson Number (R_0): $-1.0 \leq R_0 \leq 0.2$[(b)]
Surface Roughness: 0.0001 m to 1.0 m[(c)]
Ignition Source Location: Close to pool - downwind of flammable clou
Humidity: 0-100%
Ignition Type: Open flame and explosion[(d)]

Maximum volume as recommended by the 1976 LNG Safety and Control Works
DOE-EV-0002, An Approach to Liquefied National Gas (LNG) Safety and En
mental Control Research (Appendix C) February 1978.
Spans most atmospheric stability conditions.
Characterizes surfaces from smooth sea states to forests and small tow
This is achievable at forested locations near larger bodies of water s
that the wind comes over the water at times and over the forest at tim
(Surface roughness is a measure of the aerodynamic roughness of the su
face classically between 1/10 and 1/30 of the vegetation height.)
Explosion having the characteristics of that from natural gas ignited

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(Surface roughness is a measure of the aerodynamic roughness of the
face classically between 1/10 and 1/30 of the vegetation height.)
Explosion having the characteristics of that from natural gas ignit

Pool Size[a]

Land: 10-30 m diameter; (20-180 m^3)
Water: 2-1000 m^3
Wind Speed: 0-13.5 m/s (0-30 mph) measured at 9.1 m (3
Surface Roughness: 0.0001 m to 1.0 m[c]
Spill Surface: Land; water (shallow and deep)

This section presents the various experimental strategies considered
study along with an indication of their associated number of tests. T
ral categories of strategies were investigated: the classical approac
statistical screening approach, and the statistical response surface
oach. A variety of strategies are possible within the latter two cate
es. The strategies basically are differentiated by the amount of info
on they provide and by the number of independent observations required
rmine this information (i.e., the more information, the more independe
rvations required to obtain this information). In general, the screen
tegies are used to provide information on the main effects of each var
can thus detect mischaracterization of variables. There are a variety
trategies in the screening category. They are differentiated by the
er of tests required to make an estimate of the main effects of the
able. *In general the response surface strategies are used to provide*
rmation on functional dependencies and interaction of variables. Ther
also a variety of strategies in the response surface category. They a
erentiated by their differing ability to fit surfaces of complex curva
her discussion of the strategies are given in the following subsection

VAPOR GENERATION AND DISPERSION

on 6.1.a

Classical Approach

The classical approach involves varying of one parameter at a time wh
ing all others constant. A large number of experiments are required t
ne the simultaneous effects of several variables. This method is prac
laboratory experimentation where the cost of each test is not large ar
icient time is available; it was not considered practical for field
rimentation giving consideration to program constraints.

on 6.1.b

Statistical Screening Approach

Statistically based experimentation involves the simultaneous varying
ll selected experimental variables in a selected pattern based on the

able analytic methods incorrectly characterize the influence of each var

From Section 4.1, six variables should be screened for the case of spills and water spills:

- Spill Volume
- Spill Rate
- Wind Speed
- Richardson Number
- Surface Roughness
- Heat Input to Cloud

Examples of available statistical screening strategies are:[(a)]

- Plackett-Burman

  Requires 12 runs (6 at maximum size) for <u>both</u> land and water.

  Sufficient to study main effects, but provides only qualitative inf mation on interaction and no information on curvature effects.

  Sufficient runs are performed to determine mischaracterization of variable by an amount of two standard deviations or greater.

- Two-level factorial

  Requires 64 runs (32 at maximum size) for <u>both</u> land and water

  Sufficient to study main effects and interactions, but provides no curvature data

  Sufficient number of runs for significant sample

- Two-level factorial with centerpoint

  Requires 65 runs (32 at maximum size and one intermediate point for <u>both</u> land and water.

  Same advantages as two level factorial but provides qualitative information on curvature

---

(a) There are many other strategies or designs (e.g., fractional factori which could also be used. In fact, if the program constraints diffe those assumed in this document, other designs could be preferable.

cation of this strategy to the study of vapor generation and dispersion

n 6.1.c

Statistical Response Surface Approach

Statistical based experimentation involves the simultaneous varying of xperimental variables in a predescribed pattern which is selected based experimental objectives. Response surface approaches provide sufficien to develop empirical correlations and estimate experimental error. We ot interested in exact functional relationships but rather scouting for bles improperly characterized.

From Section 4.1, six variables should be considered for both land and

Spill Volume
Spill Rate
Wind Speed
Richardson Number
Surface Roughness
Heat Input to Cloud

Examples of response surface strategies are:

Box-Behnken (describes the response surface by a full quadratic polynom

Requires 54 runs (12 at maximum scale, 30 at an intermediate scale)

Three-level factorial (provides estimates of the linear, quadratic and nteraction effects for a full quadratic polynomial description of the process)

Requires 729 runs (243 at maximum size)

VAPOR CLOUD FIRES

n 6.2.a

Classical Approach

See remarks under Option 6.1.a.

See description under Option 6.1.b.

From Section 4.2, seven variables should be screened for confi
unconfined types of ignition.

- Spill Size (one surface)
- Concentration of Gas Species
- Wind Speed
- Richardson Number
- Ignition Location
- Humidity
- Surface Roughness

Examples of screening strategies include the following:

(see Option 6.1.a for advantages of each)

- Plackett-Burman

  Requires 20 tests (10 at maximum size)

- Two-level factorial

  Requires 128 runs (64 at maximum size)

- Two-level factorial with centerpoint

  Requires 129 runs (64 at maximum size)

The Plackett-Burman strategy requires the least number of runs
characterize the main effects of the variables and would provide a
cost program. This strategy is thus selected as meeting the object
the program at a minimum cost. See Table B-2 for application of th
to the study of vapor cloud fires.

Option 6.2.c

Statistical Response Surface Approach

See description under Option 6.1.c.

From Section 4.2, seven variables should be considered for co
unconfined types of ignition.

Wind Speed

Richardson Number

Ignition Location

Humidity

Surface Roughness

Examples of response surface strategies are:

Box-Behnken

Requires 62 runs (12 at maximum scale, 38 at an intermediate scale

Three-level factorial

Requires 2187 runs (729 at maximum size)

POOL FIRES

ion 6.3.a

Classical Approach

See remarks under Option 6.1.a.

ion 6.3.b

Statistical Screening Approach

See description under 6.1.b.

From Section 4.3, four variables should be screened for both land an er:

Pool Size

Wind Speed

Turbulence (Atmospheric)

Surface Roughness

Examples of screening strategies are as follows:

Plackett-Burman

Requires 12 tests (6 at maximum size)

Too few runs for significant test

- Two-level factorial with centerpoint

  Requires 17 runs (8 at maximum scale)

  Too few runs for significant test

The 12 run Plackett-Burman strategy requires the least number to characterize the main effects of the variables and would provide cost program. This strategy is thus selected as meeting the object the program at a minimum cost. Also, the 12 run Plackett-Burman pr the fewest runs with the ability to detect an effect twice as large experimental error. See Table B-3 for application of this strategy fires.

Option 6.3.c

Statistical Response Surface Approach

See description under Option 6.1.c.

From Section 4.3, four variables should be considered for both and water:

- Pool Size
- Wind Speed
- Turbulence (Atmospheric)
- Surface Roughness

Examples of response surface strategies are:

- Box-Behnken

  Requires 15 runs (4 at maximum size; 7 at an intermediate size

- Three-level factorial

  Requires 27 runs (9 at maximum scale)

This study has examined candidate experimental strategies and selec
s that seemed to best fit postulated program constraints on field exp
ectives and the time and money available for the experiments. The pr
straints clearly call for a statistical strategy. It is also clear t
y a fraction of the parameters influencing the behavior of an LNG spi
or should be, investigated in the field experiments. Which paramete
uld be investigated, over what range, and with what preciseness is no
clear. However, based on a particular set of assumptions stated in
report, a candidate statistical strategy was selected for varying
magnitude of experimental parameters (variables) associated with the
lowing three LNG release processes: (1) LNG vapor generation and
persion (2) LNG vapor cloud fires and (3) LNG pool fires.

For the LNG vapor generation and dispersion process the following s
ameters were deemed important:

Spill volume
Spill rate
Wind speed
Richardson number
Surface roughness
Heat input to cloud

A 12-run Plackett-Burman statistical screening strategy was selecte
candidate experimental matrix strategy for varying the above paramet
land and water spills, plus two scouting tests on insulated concrete
otal of 26 runs. This is sufficient to study the main effects of the
ameters and determine mischaracterization of a variable by an amount
ce the experimental error.

For the LNG vapor cloud fires the following seven parameters were c
ortant:

Spill size
Concentration of gas species
Wind speed
Richardson number

- Surface roughness

A 20-run Plackett-Burman statistical screening strategy was s
the candidate experimental matrix strategy for varying the above v
for both confined (explosive) and unconfined ignition for a total
This is sufficient to study the main effects of the parameters and
mischaracterization of a variable by an amount of twice the experi

For the LNG pool fire process the following four parameters w
important:

- Pool size
- Wind speed
- Turbulence
- Surface roughness

A 12-run Plackett-Burman statistical screening strategy was s
the candidate experimental matrix strategy for varying the above p
for both land and water for a total of 24 runs. It should also be
that two more parameters could be added to the above list without
number of tests required. The number of tests recommended is suff
study the main effects of the parameters and determine mischaracte
a variable by an amount of twice the experimental error.

This report considered several other statistical strategies s
level factorial, two-level factorial with centerpoint, Box-Behnken
level factorial strategies. The rationale for selection is covere
test under each LNG release process.

A few words are necessary on the limitations of this study.
constraints postulated in order to select between candidate strate
qualitative and reflect the author's judgements on modelers' curre
standing (basically correct) of the processes involved and the tim
money available to carry out the experimental effort. These judge
and should be reevaluated through: 1) critical examination and se
exercise of predictive models, 2) engineering analysis of the time
required to conduct the experiments, and 3) quantification of the
time and cost constraints.

behavior of LNG releases. Even using the recommended Plackett-Burma
ategy there are opportunities for reducing the number of runs and hen
time and cost for the field experiment program. For example, if it
determined by other means that an explosion will not propagate throug
vapor cloud, then the vapor cloud fire experiments with confined
ition sources can be eliminated, reducing the number of runs by 20,
the vapor cloud fire experiments, if it can be determined that only 6
ameters need to be investigated rather than 7, the number of runs cou
reduced from 20 to 12. It must be noted, however, that if, after hav
pleted the 12 runs with the 6 variables it is determined that 7 varia
uld have been considered it will require more than 8 additional runs
the information.

Another possible way to reduce the total number of experiments is t
bine experiments (e.g., conduct vapor cloud fire experiments on the s
ease after the vapor generation and dispersion data has been collecte
ever, it is not clear that this is technically feasible. Therefore,
ommended use of the results of this study is as both guidance and a
rting point for development of the final experimental strategy for th
field experiment studies.

As a final note, it must be pointed out that if the recommended
tistical approach is adopted, serious shortcomings can occur if the
ts are not performed in random order. If randomization is not used,
ge bias errors may result which could be falsely attributed to one
the variables.

APPENDIX A

RATIONALE FOR THE SELECTION, ELIMINATION OR COMBINATION OF EXPERIMENTAL PARAMETERS

This appendix provides the logic and rationale used to select, nate or combine parameters listed in Section 3. This process resul identifying a recommended set of parameters to be varied in a field program. Section 4 is a summary listing of these recommended param

Vapor Generation and Dispersion Parameters	Description of Logic Used to Select, Eliminate or Combine	Disposit
Spill Volume	Considered a Major Factor	Selected
Spill Rate	Deemed a Major Factor	Selected
Spill Shape	Fixed by Experimental Objective	Eliminat
Spill Surface	Major Factor for Heat Transfer	Selected
Air Pressure	Weak Function of ΔT	Eliminat
Thermophysical Properties	Composition of LNG is expected to be fixed	Eliminat
Ground Temperature	Available energy doesn't change much	Eliminat
Water Temperature	Available energy doesn't change much	Eliminat
LNG Composition	Fixed at nominal composition	Eliminat
Pool Depth of Water	Fix at deep depth as worst case	Eliminat
Water Characteristics	Difficult to evaluate, needs further thought; eliminated because of lack of strong argument to select	Eliminat
Wind Direction	Important only in alignment of sensors	Eliminat
Wind Speed	Important parameter in all current models	Selected
Topography	Once SEE site is selected, topography fixed	Eliminat
Structures	Fixed by experimental design	Eliminat

Source Elevation	Presently fixed at ground level	Eliminated
Water Pickup	Secondary effect	Eliminated
Temperature Lapse Rate	Factor included in number	Combined
Temperature Difference (Air, Water)	Variations in energy due to variable small	Eliminated
Temperature Difference (Air, Water)	Not believed to have significant scale dependence	Eliminated
Temperature Difference (Ground, Water)	Variations in energy due to variable small	Eliminated
Vertical Wind Shear	Factor Included in Richardson number	Combined
Wind Fluctuations (s,y,z,t)	Defined, knowing wind speed, surface roughness and Richardson number	Combined
Surface Roughness	Important parameter to define turbulence and velocity profile	Selected
LNG Pool Temperature	Variations small compared to total temperature	Eliminated
Air Temperature	Variable included in heat input to cloud	Combined
Water Temperature	Variable included in heat input to cloud	Combined
Ground Temperature	Variable included in heat input to cloud	Combined
Solar Radiation	Variable included in heat input to cloud	Combined
Cloud Temperature	Variable included in heat input to cloud	Combined
Relative Humidity	Variable included in heat input to cloud	Combined

Vapor Cloud Fire Parameters	Description of Logic Used to Select, Eliminate or Combine	Disposition
Size and Shape of Gas Cloud	Deemed important	Selected
Concentration of Gas Species	Deemed important	Selected

Vapor Cloud Fire Parameters	Description of Logic Used to Select, Eliminate or Combine	Disposition
Cloud Temperature	Variations in energy small compared to combustion energy	Eliminated
Wind Speed	Important parameter	Selected
Turbulence (Atmospheric)	Important entrainment parameter	Selected
Water Vapor	Could be important in small experiments	Selected
Other Meteorological Conditions	Considered second order effects	Eliminated
Ignition Source Type and Location	May cause major variations concerning blast effects	Selected
Topography	Second order effect	Eliminated
Structures	Fixed by design	Eliminated
Reaction Mechanics	Fixed by nominal LNG composition	Eliminated
Chemical Kinetics	Fixed by nominal LNG composition	Eliminated
Thermodynamic, Transport and Thermophysical Properties	Fixed by nominal LNG composition	Eliminated
Optical Properties	Fixed by nominal LNG composition	Eliminated

Pool Fire Parameters	Description of Logic Used to Select, Eliminate or Combine	Disposition
Pool Size	Important due to non-point source effects	Selected
Pool Shape	Fixed by design	Eliminated
LNG Composition	Fixed	Eliminated
LNG Temperature	Energy variations small compared to combustion	Eliminated
Wind Velocity	Important when wind speed is high	Selected
Turbulence (Atmosphere)	Important mixing parameter	Selected
Other Meteorological Conditions	Secondary input for large fires	Eliminated

Topography and Structures	Fixed by design	Elimin
Spill Surface (Water, Land)	Important for heat transfer	Select
Reaction Mechanisms	Fixed by initial conditions	Elimin
Chemical Kinetics	Fixed by initial conditions	Elimin
Thermodynamic Transport and Thermophysical Properties	Fixed by initial conditions	Elimin
Optical Properties	Fixed by initial conditions	Elimin

TABLE B-1. Vapor Generation and Dispersion (12-Run Plackett-Burman Test Design)

[(+) signifies maximum value of parameter and (-) signifies minimum value of parameter]

	Run[a]	Spill Volume	Spill Rate	Richardson No.	Heat Input to Cloud	Wind Speed	Sur Roug
Land	1	+	+	-	+	+	
	2	+	-	+	+	+	
	3	-	+	+	+	-	
	4	+	+	+	-	-	
	5	+	+	-	-	-	
	6	+	-	-	-	+	
	7	-	-	-	+	-	
	8	-	-	+	-	+	
	9	-	+	-	+	+	
	10	+	-	+	+	-	
	11	-	+	+	-	+	
	12	-	-	-	-	-	
Water	1	+	+	-	+	+	
	2	+	-	+	+	+	
	3	-	+	+	+	-	
	4	+	+	+	-	-	
	5	+	+	-	-	-	
	6	+	-	-	-	+	
	7	-	-	-	+	-	
	8	-	-	+	-	+	
	9	-	+	-	+	+	
	10	+	-	+	+	-	
	11	-	+	+	-	+	
	12	-	-	-	-	-	
ulated crete	1[b]	-	+	+	+	-	
	2[b]	-	-	+	-	+	

Runs must be performed in random order.

"Scouting Tests" selected at random.

Burman Test Design)*

[(+) signifies maximum value of parameter and
(-) signifies minimum value of parameter]

Run (a)	Size Spill	Wind Speed	Richardson No.	Ignition Location	Concentration of Gas Species	Humidity	Surface Roughness
1	+	+	-	-	+	+	+
2	+	-	-	+	+	+	+
3	-	-	+	+	+	+	-
4	-	+	+	+	+	-	+
5	+	+	+	+	-	+	-
6	+	+	+	-	+	-	+
7	+	+	-	+	-	+	-
8	+	-	+	-	+	-	-
9	-	+	-	+	-	-	-
10	+	-	+	-	-	-	-
	-	+	-	-	-	-	+
	+	-	-	-	-	+	+
	-	-	-	-	+	+	-
	-	-	-	+	+	-	+
	-	-	+	+	-	+	+
	-	+	+	-	+	+	-
	+	+	-	+	+	-	-
	+	-	+	+	-	-	+

(-) signifies minimum value of parameter]

	Run(a)	Pool Size	Wind Speed	Turbulence	Richards Number
Land	1	+	+	-	+
	2	+	-	+	+
	3	-	+	+	+
	4	+	+	+	-
	5	+	+	-	-
	6	+	-	-	-
	7	-	-	-	+
	8	-	-	+	-
	9	-	+	-	+
	10	+	-	+	+
	11	-	+	+	-
	12	-	-	-	-
Water	1	+	+	-	+
	2	+	-	+	+
	3	-	+	+	+
	4	+	+	+	-
	5	+	+	-	-
	6	+	-	-	-
	7	-	-	-	+
	8	-	-	+	-
	9	-	+	-	+
	10	+	-	+	+
	11	-	+	+	-
	12	-	-	-	-

s must be performed in random order.

REPORT P

Annotated Bibliography LNG Safety and Environmental Control Research

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Pacific Northwest Laboratory
Richland, Washington 99352
Operated by Battelle Memorial Institute
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Battelle Columbus Laboratories

SUMMARY

This bibliography provides brief summaries of literature related to safety and environmental control, organized alphabetically by author. A supplemental listing, also alphabetical by author, begins on page 7.

Report on LNG Safety Research, Vol. I. Report by Arthur D. Little, Ir
A.G.A., January 31, 1971. A.G.A. Project I U-2-1, A.G.A. Catalog No.
9711.

It is concluded that smaller releases are rather rare and usually not damaging; probability is low that a large spill will occur from currently constructed facilities; spills from containers may have acceptable probability but some additional protection should be provided; risk of transfer line failure requires higher level of protection; further consideration should be given to hazards involved with LNG transport.

ger, A. S., Corlett, R. C., Gordon, A. S. and Williams, F. A., Some As
Structures of Turbulent Pool Fires. WSS/CI 76-46, October 1976.

Results are reported on the burning of JP-5 and methanol pools 305 cm in dia. Measurements made include radiant energy fluxes outside and within the fire, temperatures and chemical compositions within the fire and rates of weight loss of the pool. Results emphasize structural differences between JP-5 and methanol fires and importance of radiant feedback of energy to the pool surface in controlling rates of burning.

lan, D., Atallah, S., Drake, E., Hinckley, R., Mathias, S., Technology
d Current Practices for Processing, Transferring and Storing Liquefie
tural Gas. Department of Transportation/OST, Office of Pipeline Safe
shington, DC, (prepared by Arthur D. Little, Inc., Report No. C-76971
cember 1974.

Current state-of-the-art safety information related to the design, location, construction, operation and maintenance of facilities required for liquefaction, transfer, storage, and revaporization o natural gas is assembled and summarized. A detailed review of code standards and practices pertaining to LNG installations is present along with an evaluation of present trends in LNG safety requireme LNG safety research programs completed or in progress are describe and key research results summarized. Finally a methodology for quantitative assessment of risks associated with LNG facilities is outlined.

ngren, D. W. and Smith, J. L., Jr., "The Inception of Nucleate Boilin
th Liquid Nitrogen." Journal of Engineering for Industry. pp 1211-1
vember 1969.

The phenomena of patchwise boiling are discussed, and the signific parameters restricting the growth of a boiling patch are analytica determined to be: a high nucleate boiling heat-transfer coefficie

Anderson, R. P. and Armstrong, D. R., "Experimental Studies of Vapor
3rd International Conference on Liquefied Natural Gas, paper 3 of Ses
Chicago, 1972.

Small scale experiments with molten salts and molten metals, inj into water, are described. In some cases ensuing reactions can into vapor explosions.

An Experimental Study of the Mitigation of Flammable Vapor Dispersion Fire Hazards Immediately Following LNG Spills on Land. A report by University Engineers, Inc., to the American Gas Association, February

A series of fire control, fire extinguishment and vapor dispersi tests were conducted under the high boil-off rates which occur immediately following an LNG spill on land. Correlations of the results provide fire control and extinguishment times with dry c ical agents and high expansion foams. The magnitude of the redu in downwind concentrations of methane vapors by the application high expansion foam on the spill was also determined.

Analysis of Risk in the Water Transportation of Hazardous Materials, Coast Guard Report, CG-D-39-76. NTIS No. AD/A025298, January 1976.

This report assesses the utility and feasibility of using risk analysis to assist in management decisions regarding the regulat of water transportation of bulk hazardous materials. A number o risk analysis studies were surveyed. Barge transportation on inland waterways was chosen for special study, and a probabilist model of risk was selected. It was concluded that the greatest utility of the methodology lies in answering specific questions with output of a specific predetermined nature.

Andersen, W. H., Garfinkle, D. R., Carpenter, G. E. and Brown, R. E., Absorption Near and Below the Burning Surface of Hydrocarbon Pools." presented at the 1969 Meeting, Central States Section, The Combustion Institute, March 18-19, 1969.

The burning behavior of a liquid fuel pool is discussed in terms the heat feedback from the flame that is transported into and th the fuel via conduction and radiation. It is shown that the rad flux contribution to the total heat flux input is greatest for b zene, and decreases consecutively for gasoline, kerosine, and al

Anderson, R. P. and Armstrong, D. R., "Experimental Study of Vapor Ex Paper presented at the Third International Conference and Exhibition Liquefied Natural Gas, September 24-28, 1972, Washington, DC.

Present knowledge about various aspects of vapor explosions is summarized. Particular emphasis is placed on methods of evaluat the destructive kinetic energy release from a specified accident A theoretical method of calculating the maximum destructive ener is outlined.

Andrews, G. E. and Bradley, D., "The Burning Velocity of Methane-Air
Combustion and Flame. 19:275-288, 1972.

Results are presented for the variation of burning velocity wit equivalence ratio for methane-air mixtures at one atmosphere pr Values were determined by the bomb-hot wire and corrected densi ratio techniques, for combustion during the pre-pressure period The former of these methods gives a maximum burning velocity of 45 ± 2 cm/sec, at an equivalence ratio of 1.07.

Anthony, E. J. "Some Aspects of Unconfined Gas and Vapor Cloud Explo
Journal of Hazardous Materials, 1: 284-301, 1975-77.

A critical review is presented of experimental and theoretical work on unconfined vapor explosions with emphasis on modeling studies.

Atallah, S. and Allen, D. S., "Safe Separation Distances From Liquid Spill Fires." Paper presented at Central States Section, Combustion Meeting on Disaster Hazards, Houston, TX, April 1970.

This paper critically reviews the methods generally used to cal culate safe separation distances from liquid fuel spill fires. Correlations for predicting flame height and other radiative pr erties are reviewed. Distances at which the thermal radiation flux falls below the minimum level needed to ignite cellulosic materials are calculated and the results are presented in conve graphical form.

Atallah, S. and Raj, P., "Thermal Radiation From LNG Spill Fires." P-3 presented at the Cryogenic Engineering Conference, Atlanta, GA, August 10, 1973.

This paper reviews the present state of knowledge relating to thermal radiation from LNG fires. Utilizing data from recent AGA-sponsored LNG fires in seven 6-ft, six 20-ft, and one 80-ft diameter pools, equations were derived for predicting LNG flame height and the angle of tilt of LNG flames in the presence of wind. A model for predicting the thermal radiative flux at various locations away from an LNG fire is presented.

Baitis, A. E., Bales, S. L. and Meyers, W. G., Prediction of Lifetim Accelerations for Design of LNG Cargo Tanks, Coast Guard Report CG-D NTIS No. AD1779635, March 1974.

A procedure is developed to predict the extreme accelerations needed for design of the cargo tanks in LNG vessels. The valid of the prediction tool is discussed. Comparisons are made with accelerations measured in model and full scale experiments.

The results of a pilot study on a single, large typical LNG ship are presented. Acceleration response variations due to changes in ship load conditions and changes due to longitudinal, lateral and vertical locations are examined.

Beer, J. M., "Methods for Calculating Radiative Heat Transfer from Flames Combustors and Furnaces." Heat Transfer in Flames. Chapter 2, John Wiley and Sons, 1974.

Recent advances in methods for predicting radiative heat flux distribution in furnaces and combustors are reviewed with special reference to the zone method of analysis and the flux methods. Recent experimental studies specially designed to test these prediction procedures under sufficiently severe conditions are discussed.

Bellus, F., Cochard, H. Cochard, Vincent R., Mauger, J., Controlling the Hazards from LNG Spills on the Ground LNG Firefighting Methods and Their Effects Application to Gaz de France Terminals. Gaz de France, DOE-Tr-18

Three basic areas are examined in this paper. A mathematical model to calculate vapor dispersion from accidental LNG spills on land is described. This model is used to investigate various types of impounding areas and their minimization of methane cloud travel. A method to calculate water spray rates for the protection of LNG tank walls from the energy radiated by an adjacent fire is described and a numerical example is given. The authors describe the details of design and construction of the new 80,000 m^3 LNG tank at the Fos Terminal.

Bensesh, M. E. , "The Use of Gas Hydrates in Improving the Load Factor of Gas Supply Systems." U.S. 2,090, 163 (to Chicago By-Products Corp), 1942

This method recommended using excess natural gas, during low demand periods, for hydrate formation and storage. The natural gas would be regenerated for peak demand.

Blinov, V. I. and Khudyakov, G. N., "Certain Laws Governing Diffusion Burning of Liquids." Doklady Akademii Nauk S.S.S.R. 113:1094-1098, 1957.

An investigation of the burning of gasoline, diesel oil, solar oil and a number of other petroleum products in containers having different diameters enabled the authors to determine some important relationships for diffusion of burning liquids.

Board, S. J., Farmer, C. L. and Poole, D. H., "Fragmentation in Therm
Explosions." International Journal of Heat and Mass Transfer. 17:33
1974.

Experiments involving explosions between molten tin and water ar described. Results indicate that thermal explosions usually inv several distinct interactions; a small disturbance can escalate successive growth and collapse cycles; vapour collapse is the ma cause of dispersion in many thermal explosions, and the jet pene tion hypothesis can account for both the time scales and energy transfer rates.

Boyle, G. J., "Vapor Production From LNG Spills on Water." American
Association Distribution Conference, May 1973.

The results indicate that LNG spilled onto water will spread out with a rate that decreases with time; vapor production will equa the discharge rate as long as the discharge is occurring; with a batch spill it is necessary to take into account the LNG which e rates to calculate the maximum pool and the peak vapor productio rate; the dispersion plume from a large LNG spill on water will wide and shallow.

Boyle, G. J. and Kneebone, A., Laboratory Investigation into the Char istics of LNG Spills on Water, Evaporation, Spreading and Vapor Dispe Re 6Z32, Shell Research Limited, Released by the American Petroleum I tute, March 1973.

This is a laboratory and small-scale wind tunnel investigation o the characteristics of LNG spills on water. One characteristic investigated, that has not been studied by others, is the apprec incorporation of water in the vapor cloud.

Brown, L. E., Martinsen, W. E., Muhlenkamp, S. P. and Puckett, G. L., Scale Tests on Control Methods for Some Liquefied Natural Gas Hazards Report, prepared by University Engineers, Inc., Norman, Oklahoma, for U.S. Coast Guard, Report Numbers CG-D-95-86 and AD-A033 522, May 1976

A report of results of small scale (100 ft^2) tests of some lique natural gas (LNG) hazard control methods and concepts. Tests of water spray screens showed that the concept is practical and eff for small LNG spills. Tests of water spray screens to reduce ra heating of exposures demonstrated no practical value.

ıstowski, T. A., "A New Criterion for the Length of a Gaseous Turbulent
fusion Flame." Combustion Science and Technology. 6:313-319, 1973.

The flame tip is identified with the point on the axis of maximum fuel concentrations where the fuel has been diluted to the lean flammability limit. Flame-length equations are derived using the new criterion, together with data from the literature on entrainment of air into flames, transverse concentration profiles in turbulent jets, and flammability limits.

ıstowski, T. A., "The Hydrocarbon Turbulent Diffusion Flame in Subsoni
ss-Flow," AIAA Paper 77-222, January 1977.

The flame is modeled as a bent-over initially vertical circular jet with top-hat profiles of composition, temperature, and velocity. The hydrocarbon pyrolyzes in a zero-order reaction and the pyrolysis products are oxidized at a rate proportional to the rate of entrainment of air into the flame.

gess, D., Biordi, J. and Murphy, J., Hazards of Spillage of LNG into W
RC Report No. 4177, U.S. Department of the Interior, Bureau of Mines,
tsburgh, PA, 1972.

These are reports of experimental investigations of LNG spills on water. The pool spread, evaporation rate, vapor gravity spread, downwind drift and dispersion were studied in spill sizes up to 0.5 m^3. In unconfined spills coherent ice flow formation was not observed. In several cases small scale physical explosions were observed but no attempt was made to study the initiation or burning of the cloud.

gess, D. S. and Hertzberg, M., "Radiation From Pool Flames." Heat Tra
Flames. Chapter 27, John Wiley & Sons, 1974.

Some radiation data from pool flames is summarized and our understan ing of the problem is reviewed. Spectral data yield a 1500° K temperature for hydrocarbon pool fires, which is consistent with the 40 percent maximum in the fraction of combustion energy radiated, an with limited flame temperatures for the mixing limited systems. A revised correlation of mass burning rate with $\Delta H_c/\Delta H_v$ is presented, and derived fundamentally.

gess, D. S., Murphy, J. N. and Zabetakis, M. S., Hazards Associated wi
Spillage of Liquefied Natural Gas on Water. Report RI 7448, U.S. Dep
t of the Interior, Bureau of Mines, November 1970.

The hazard of spilling LNG onto water is discussed. After spillage, the initial vaporization rate of LNG was determined to be 0.037 lb/ ft^2 sec. If the LNG was confined, this rate was modified by the formation of ice on the water surface. Using a 2000-gallon LNG sample, the maximum diamter (in feet) of the spreading pool was calc

ess, D. S., Murphy, J. N. and Zabetakis, M. S., Hazards of LNG Spilla
arine Transportation Final Report. NTIS No. AO-70578, for USCG, Offi
esearch Development, February 1970.

The hazard of spilling LNG onto water is discussed. After spillage onto water, the initial vaporization rate of LNG was determined to be 0.037 lb/ft^2 sec. If the LNG was confined, this rate was modified by the formation of ice on the water surface. Using a 2000-gal LNG sample, the maximum diameter (in feet) of the spreading pool was calculated at 6.3 $W_o^{1/3}$ where W_o is the weight of LNG in pounds.

ess, D. S., Strasser, A. and Gumer, J., "Diffusive Burning of Liquid
s in Open Trays." Fire Research Abstracts and Reviews. 3(3):177-192
.

The paper describes the effects of fuel temperature and wind on burning rate, discusses the problem of cryogenic fuels, and suggests that burning rate may be predicted from heats of vaporization and combustion of the fuel. Data on methanol, LNG, liquid hydrogen, amine fuels, and typical hydrocarbons are included.

ess, D. S. and Zabetakis, M. G., Detonation of a Flammable Cloud Foll
Propane Pipeline Break: The December 9, 1970 Explosion in Port Hudso
ouri. U.S. Department of the Interior, Bureau of Mines, RI-7752, 197

This report summarizes the incidents that preceded the December 9, 1 propane-air explosion in Port Hudson, MO. Both near- and far-field damage indicated that this explosion may be attributed to the detonation of propane in air with an energy release equivalent to that fro about 50 tons of detonating TNT.

ess, D. and Zabetakis, M. G., Fire and Explosion Hazards Associated W
efied Natural Gas. U.S. Department of the Interior, Bureau of Mines,
099, 1962.

Factors that should be considered in evaluating the fire and explosion hazards relating to any fuel are discussed. These factors are utilized in the design of experiments to evaluate the hazards associated with LNG as compared to those hazards associated with other fuels.

hmann, C. H., "Experiments on the Dispersion of Heavy Gases and Abate
of Chlorine Clouds." Proceedings of the Fourth International Sympos
ransport of Hazardous Cargoes by Sea and Inland Waterway, Jacksonvill
October 26-30, 1975, Report No. AD/A-023 505, pp 475-488, October 197

The experiments comprised four different parts: dispersion of heavy gases offer an instantaneous release; penetration of heavy gases in

Byram, G. M., "Scaling Laws for Modeling Mass Fires." Pyrodynamics. 4:271-284, 1966.

The paper is concerned with the development of scaling laws necessary for modeling and is restricted to the stationary mass fire.

Byram, G. M. and Nelson, R. M., Jr., "Buoyancy Characteristics of a Fir Source." Fire Technology. 10(1):68-79, 1974.

Buoyancy production rates for a pure heat source and for a fire he source of burning woody fuels show that fire may be regarded as a pure source yielding heated air rather than heated combustion prod

Byram, G. M. and Nelson, R.M., Jr., "The Modeling of Pulsating Fires." Technology. 6(2):102-110, 1970.

The authors present scaling relationships for modeling pulsating fires. Data gathered from various sizes of pulsating fires compared favorably with the predicted relationships between fire diameter and pulsation frequency.

Cahn, R. P., Johnston, P. H. and Plumstead, J. A., "Transportation of Natural Gas Hydrate." U.S. 3,514,274 (to Esso Research and Engineering Co.), 1970.

Natural gas was combined at 25 to 40°F and >80 psia with a slurry of propane hydrate in propane. This mixture was cooled to -40°F to give methane hydrate slurry in propane. Treating this product with propane gas at 25-40°F and <80 psia regenerated methane and propane hydrate.

Carne, M., Thomas, J. R. and Hutchinson, E. A., Buxton Bund-Fire Tests. Gas Council, December, 1971.

Ignition and burnout tests were conducted on LNG contained within walls of clay or pulverized fuel ash. The test objective was to establish whether walls of this construction would be damaged by a combination of cold LNG and flame radiation. Results showed no damage to the walls apart from a superficial calcining of the turf and slight spalling of the concrete covering. Flame radiation agreed reasonably well with predicted values.

Cermak, J. E., "Applications of Fluid Mechanics to Wind Engineering - A man Scholar Lecture." Journal of Fluids Engineering. 97:9-38, March 1

The objectives of this review are to establish an initial subject-matter base for wind engineering, to demonstrate current capabilit and deficiencies of this base for an engineering treatment of wind effect problems, and to indicate areas of research needed to broad and strengthen the subject-matter base.

hatterjee, N. and Geist, J. M., Spontaneous Stratification in LNG Tanl
ontaining Nitrogen. ASME Publication 76-WA/PID-6, December 5, 1976.

LNG containing significant concentrations of nitrogen can stratify spontaneously during weathering in storage tanks. Mixing of strat fied layers leads to an increase in boil-off rates, commonly refer red to as "rollover". LNG storage tanks can be designed and opera safely if stratification and associated problems are taken into account.

hatterjee, N. and Geist, J. M., "The Effects of Stratification on Boi ates in LNG Tanks." Paper presented at the A.G.A. Distribution Confer tlanta, GA, May 8-10, 1972.

The addition of LNG to a partially filled tank containing liquid c a different density may lead to the temporary formation of stratif layers. The physical phenomena associated with the mixing of stra fied layers of LNG have been simulated on the computer. One metho for mitigating potential hazards associated with stratification is limiting the density and the temperature difference between fresh liquid and LNG in the tanks.

lapp, M. B. and Litziner, L. F. "Marine Terminals for LNG, Ethylene, a PG." A paper presented at the 68th National AICHE Meeting, Houston, 1 ebruary 28 - March 4, 1971.

The design and economics of marine terminals for LNG, Ethylene, ar LPG are discussed. Some discussion of safety features is includec

losner, J. J. and Parker, R.O., "A Careful Accident Assessment Key to torage Safety." Oil and Gas Journal. pp 47-51, February 6, 1978.

This article discusses potential accidents and related hazards ass ciated with LNG storage facilities. A list of mitigating measures which would prevent an accident or reduce its consequences is inc

losner, J. J. and Parker, R. O. "Safety of Storage Designs Compared." nd Gas Journal. pp 121-125, February 13, 1978.

Eight different types of LNG storage designs are compared with res to the likelihood and potential consequences of a spill or accider

olgate, S. A. and Sigurgeirsson, T. "Dynamic Mixing of Water and Lava. ature. 244:552-555, August 31, 1973.

It is suggested that lava eruptions under the ocean might result vapor explosions, similar to those which have been observed when liquid metals or LNG come into contact with water. Violent mixing of water and lava are believed to be the cause of such explosions.

Corlett, R. C., "Gas Fires With Pool-Like Boundary Conditions: Further Results of Interpretation." Combustion and Flame. 14:351-360, 1970.

A circular, upward-facing burner, supplying uniform flux of fuel gas from a water-cooled surface, preserves the essential features of a pool fire. Addition of up to 2% methyl bromide to several fuels had no effect on heat transfer. At high fuel supply rates, the data tend to correlate independently of the air requirement of the fuel; at low supply rates, the data tend to correlate independently of volumetric supply rate.

Corlett, R. C. and Fu, T. M., "Some Recent Experiments With Pool Fires." Pyrodynamics. 4:253-269, 1966.

Steady burning rates of methanol, ethanol and acetone in thin-wallc stainless steel burners of 0.6 to 30 cm diameter have been studied. Radiation levels were estimated and are found consistent with resul of earlier experiments with water-cooled gas burners. Measured wat absorption rates are in reasonable agreement with those inferred from burning rate data on the basis of heat and mass transfer simil

Crawford, D. B. and Eschenbrenner, G. P., "Heat Transfer Equipment for L Chemical Engineering Progress, September 1972.

This article describes liquefaction heat exchangers and vaporizers for LNG facilities. Advantages, disadvantages, and relative costs for each type are included.

Crouch, W. W. and J. C. Hillver, "What Happens When LNG Spills?" Chem. 2 (4):210-215, 1972.

Authors try to assuage certain exaggerated fears about the safety hazards of LNG spills. They stress, however, the need for more information on the behavior of large spills.

Culbertson, L. and Emergy, W. B., "Liquefaction Plant Experience at Lena Presented at the 3rd International LNG Conference and Exhibition, Washir September 24-28, 1972.

This paper reviews the more significant problems encountered and solutions employed in the operation of the Alaska to Japan LNG project. This is a follow-up to earlier papers describing design and startup at the Kenai plant.

Deaton, W. M. and Frost, E. M., "Gas Hydrate Composition and Equilibriur Data." Proc. Natural Gas Department, American Gas Association. 49-56,

Phase diagrams as well as equilibrium data were presented.

Del Tatto, D. L., "LNG Satellite Peakshaving." Presented at the AGA Dis
Conference, Houston, Texas, May 6-9, 1968.

This paper presented by an engineer from Chicago Bridge and Iron describes one of the first LNG satellite operations in the U.S. Both primary liquefaction and peakshaving plant and the satellite peakshaving facility are discussed.

Department of Transportation, Liquefied Natural Gas Facilities, (LNG); "
Safety Standards: Development of New Standards," Federal Register, Thur
April 21, 1977. pp 70776-70800.

The article sets forth proposed safety standards for LNG facilities The proposed rules are based largely on National Fire Protection Association Rules (NFPA 59A (1975) and an Arthur D. Little Report summarizing LNG Technology.

Devanna, L. and Doulames, G., "Planning is the Key to LNG Tank Purging,
and Inspection." Oil and Gas Journal, pp 74-82, September 8, 1975.

Procedures used by the Lowell Gas Co. to purge a one billion cu-ft tank out of service are described in detail. The article includes a drawing showing the piping, valves, and fittings on the tank whic are used for purging.

Di Napoli, R. N., "Design Needs for Base-load LNG Storage, Regasificatio
Oil and Gas Journal. pp. 67-70, October 22, 1970.

Design of base-load storage and vaporization equipment and faciliti is described. The article contains particularly good information o the operation and control of sendout pumps and seawater vaporizers.

Dincer, A. K., Drake, E. M., and Reid, R. C., "Boiling of Liquid Nitroge
Methane on Water. The Effect of Initial Water Temperature." Int J. Hea
Transfer, pp. 176-177, 1977.

This note reports on the results of studies carried out in a vessel equipped to measure the temperature-time history at a number of locations in the bulk water phase as different cryogens were spille on the surface. It is concluded that if the initial water temperat is low, heat transfer to the cryogen occurs through a growing ice shield, with little effect on the underlying water. If the water is initially warm, ice forms more slowly and cool surface water is mixed through the bulk.

Drake, E. M., "LNG Rollover--Update." Hydrocarbon Processing. 55:119-12
January, 1976.

The article considers LNG density, effects preceding rollover, rollover time prediction, heat storage, and discusses three documented cases of rollover.

Drake, E. M., Geist, J. M. and Smith, K. A., "Prevent LNG Rollover." Hyd
carbon Processing. 52:87-90, March 1973.

Studies were undertaken of basic mechanisms involved in LNG "roll-over", to predict when they may occur and to evaluate effectiveness of possible preventive measures. Such measures include mixing durin filling, limiting variations in LNG composition and lowering tank set point pressure.

Drake, E. M., Jeje, A. A. and Reid, R. C., "Transient Boiling of Liquefie Cryogens on a Water Surface. I - Nitrogen, Methane, and Ethane." International Journal of Heat Mass Transfer. 18:1361-1368, 1975.

The results of an experimental study of the transient boiling rates of pure liquefied nitrogen, methane, and ethane in water are discuss Nitrogen boiled with the lowest heat flux rate and the highest vapor superheat. For nitrogen, the heat flux rate was found to be proportional to the square root of the liquid head. The heat flux rate fc ethane was the lowest and that for methane was intermediate.

Drake, E. M., Jeje, A. A. and Reid, R. C., "Transient Boiling of Liquefie Cryogens on a Water Surface. II Light Hydrocarbon Mixtures." Internatio Journal of Heat Mass Transfer. 18:1369-1375, 1975.

Light hydrocarbon mixtures similar to liquefied natural gas were boiled on a water surface. The rate of vaporization was measured and the heat fluxes were found to be much higher than that measured for pure liquid methane. Like methane, the rate of vaporization increased during the course of the experiment unless a continuous thick ice layer formed. No significant vapor superheat was noted.

Drake, E. M. and Reid, R. C., "How LNG Boils on Soils", Hydrocarbon Proce
54(5):191-194, May 1975.

Implications of the paper are that: boil rates of LNG on compacted soils are influenced by soil type, moisture content and LNG composition; reduction in boiling rates can be obtained by sealing the dike surface; dikes of crushed rock or stone will have higher evaporization rates than compacted soil dikes; more studies are needed to assess insulating or sealing materials under LNG spill conditions and on LNG foaming behavior.

ke, E. M. and Wesson, H. R., "Review of LNG Spill Vapor Dispersion and e Hazard Estimation and Control Methods." Proceedings of A.G.A. Trans sion Conference, Las Vegas, NV, May 1976.

This paper reviews techniques presently being used by the LNG indus for evaluating potential LNG vapor dispersion and fire hazards and will describe practical methods for reducing the severity of LNG spill accidents.

kham, H. E., "LNG Import Terminal Design Considerations." Cryogenics ustrial Gases, pp 41-48, September/October 1972.

This article describes the many processes and mechanical parameters involved in the design of an LNG import terminal. Included are discussions on facilities location, transfer lines, insulation, storage tanks, vapor handling systems, and LNG vaporizers.

fy, A. R., Gideon, D. N. and Putnam, A. A., Comparison of Dispersion Spills over Land and Water. Draft Report Prepared by Battelle Columb oratories for the American Gas Association, December 28, 1973.

This study examines and compares the available data on dispersion from land and water spills, and explains similarities and differences in results on the basis of differences in experimental techniques and test conditions, and possible differences in pertinent phenomena.

fy, A. R., Gideon, D. N., Putnam, A. A. and Bearint, D. E., LNG Safet gram - Phase I - Potential LNG Spills. Report by Battelle Columbus oratories and University Engineers, Inc., to the American Gas Associa n, February 25, 1971.

The report presents data on known spills of LNG or other cryogens, a discussion and analysis of problem areas, and a discussion of consequences of spills including downwind dispersion, radiation from fires, and reactions with water. Conclusions are summarized and recommendations made for future research.

n, W. A. and Tullier, P. M., Spill Risk Analysis Program Phase II hodology Development and Demonstration, NTIS No. AD/785026, August 19

This report describes research and results in the development and demonstration of systematic methods of assessing the effectiveness of either proposed or recently implemented merchant marine safety regulations. The methods have been designed primarily to assist Coast Guard regulatory decision-makers in their selection of altern tive means of reducing marine transportation casualties and spills of hazardous or polluting materials.

urr, C. A. and Crawford, D. B., "LNG Terminal Design." Hydrocarbon Proc
ing, November 1973.

This article discusses the special problems associated with design of an LNG terminal. Particular attention is given to the transfer line and the vapor handling and pressure control system.

urr, C. A., "Process Techniques and Hardware Uses Outlined for LNG Regas
ation." Oil and Gas Journal. May 13, 1974.

The following components of an LNG terminal are discussed by a proce engineer from M. W. Kellog: LNG unloading, storage, vapor handling, sendout pumps, vaporizers, power generation, nitrogen system, and heat recovery.

cosystems, Inc., Expected Behavior of an LNG Release Under Specified Con
eport to Federal Power Commission, August 17, 1973.

The report comprised an assessment of hypothetical LNG spill situations in the Staten Island area. Results were calculated using methods of the Esso Research and Engineering Company. Three tasks described are analyses of a 100,000 m^3 spill over water, analyses of evaporation and dispersion following an LNG tank roof failure, and a description of the New York Harbor climate.

nger, T., "Explosive Boiling of Liquefied Gases on Water." Conference P
ceedings on LNG Importation and Terminal Safety. Boston, MA, June 13-14,

Explosive boiling of a liquefied gas mixture such as LNG on ambient water can only be produced when the methane content is less than 40 mole percent. The potential hazard of having explosive boiling from an LNG spill is negligible during commercial transportation of LNG. In addition, energy estimates show that the potential damage from explosive boiling of a liquefied gas is minimal.

nger, T. and Hartman, D. E., "Mechanics of the LNG-Water Interaction."
aper presented at the American Gas Association Distribution Conference,
tlanta, GA, May 8, 1972.

Shell Pipe Line Labs has conducted research since 1970 on rapid phase transformation which can occur when LNG is spilled onto water. "Explosive" LNG-water interaction results because of rapid phase transformation and violent expansion of a thin layer of superheated LNG at the interface between the LNG and water. It is stated that "explosions occur only when LNG is a weathered state, i.e., when the methane content of LNG is less than 40 mole percent."

ger, T. and Hartman, D. E., "Rapid Phase Transformation During LNG Spi
 Water," Paper presented at the Third International Conference and Exh
on on LNG, Washington, DC, September 24-28, 1972.

It is shown that "explosions" can only occur with "aged" LNG which contains less than 40 mole percent methane. The "explosive" interaction between a liquefied gas and water is caused by the rapid phase transformation and violent expansion of a thin layer of super heated liquefied gas at the liquefied gas-water interface.

ger, T., Hartman, D. E. and Seymour, E. V., "Explosive Boiling of Liqu
ed Hydrocarbon/Water Systems." Paper presented at the Cryogenic Engin
g Conference, National Bureau of Standards, Boulder, CO, August 9-11,

The conditions which produce "explosions" when LNG is spilled on water at ambient temperature have been isolated and verified experi mentally. It has been shown that "explosions" can only occur with "aged" LNG which less than 40 mole percent methane. Contact betwee water and LNG with more than 40 mole percent methane produces norma vaporization.

gland, W. G., Teuscher, L. H., Hauser, L. E., Freeman, B. E., Atmosphe
spersion of Liquefied Natural Gas Vapor Clouds Using Sigmet, a Three
mensional Hydrodynamic Computer Model. Procedures of the 1978 Heat Tr
d Fluid Mechanics Institute. Washington State University, Pullman, WA
ne 26-28, 1978.

The SIGMET dispersion model is presented in the form that it is applied to LNG vapor dispersion problems. Model results are presented for examples of plume behavior and to verify model predictions. Model numerical methods are also described.

cudier, M. P., "Aerodynamics of a Burning Turbulent Gas Jet in a Cross
mbustion Science and Technology. 4:293-301, 1972.

The study extends the entrainment theory for weak plumes by includi into its framework the influences of radiative thermal-energy trans large density variations, and thermal-energy generation through chemical reaction. Thermal radiation is found to be of secondary importance to plume dynamics. Calculations show that a plume's motion is not significantly influenced by buoyancy forces until well downstream of the reaction zone.

Evaluation of LNG Vapor Control Methods. Report to the American
by Arthur D. Little, Inc., Cambridge, Massachusetts, October 197

It is shown that, for the high spill rates, the maximum dow hazard zone is not significantly affected by shutdown of th in the 10-minute period specified in the NFPA Code. To be in reducing downwind hazards shutdown of the leak should be shed as soon as possible, preferably under 2 minutes.

Fannelop, T. K. and Waldman, G. D., "The Dynamics of Oil Slicks Crude'." AIAA Paper No. 71-14 presented at the AIAA 9th Aerospa Meeting, New York, New York, January 25-27, 1971.

The spread of an oil slick into calm water is considered fr theoretical viewpoint. The equations of motion are derived the gravity-inertial and gravity-viscous flow regimes. For two-dimensional and radial slicks, similarity solutions are for the two flow regimes which give adequate agreement with experimental data.

Farley, M., "The LNG Plant Design Engineer." LNG/Cryogenics, pp February/March 1973.

This article, through interviews with six individuals invol LNG plant design activities, provides a brief overview of s the problems they have had to cope with on various projects

"Fast LNG-leak Detector Developed." Oil and Gas Journal. pp. 5 1977.

A new device developed and patented by the Direction of Stu New Techniques of Gaz de France is claimed to provide fast and location of leaks in large storage tanks. The location detector, at the bottom of the annular space between the wa next to the internal tank, was determined following tests m reduced model tank.

Fauske, H., "The Role of Nucleation in Vapor Explosions." Trans the American Nuclear Society. 15:813-815, 1972.

The paper suggests a possible mechanism for vapor explosion examines the validity of the mechanism in light of availabl mental facts.

Fay, J. A., "Unusual Fire Hazard of LNG Tanker Spills." Combust and Technology. 7:47-49, 1973.

This report gives theoretical expressions for the pool spre evaporation rate of liquefied natural gas spilled on water, tational spread, and the heating and downwind spread of the It does not treat the diffusion or mixing of the vapor with

y, J. A. and Lewis, D. H., Jr., "The Inflammability and Dispersion of G Vapor Clouds." Proceedings of the Fourth International Symposium on ansport of Hazardous Cargoes by Sea and Inland Waterway, Jacksonville tober 26-30, 1975, NTIS Report No. AD/A-023 505, pp 489-498, October

The paper considers the statistical properties of LNG vapor concen tration, the mean vapor concentration in dispersing cloud and downw distances for two flammability conditions.

y, J. A. and Lewis, D. H., "Unsteady Burning of Unconfined Fuel Vapor th International Symposium on Combustion, 1976.

The problem of fireball hazards associated with LNG and LPG spills investigated. A derivation of fireball maximum radius, height abo surface and time required, are obtained by phenomenological, empir and dimensional (with some physical and mathematical) analysis. Experimental corroboration is included.

ldbauer, G. F., Heigl, J. J. and McQueen, W. et al., Spills of LNG on porization and Downwind Drift of Combustible Mixtures. Report No. EE so Research and Engineering Company, May 24, 1972.

A total of seventeen LNG spill tests, ranging in size from about 2 to 2500 gallons, were carried out under a variety of weather condi The main thrust of the experimental work was aimed at measuring th parameters required to predict downwind concentrations. The aim o the experimental work was to measure the plume shape and other inf mation which would permit the data on these variables to be extra-polated.

lske, J. D. and Tien, C. L., "Calculation of the Emissivity of Lumino ames." Combustion Science and Technology. 7:25-31, 1973.

A simple analytical basis for determining the total emissivity of luminous flames is developed. The analysis considers flames whose dominant emitting species are water vapor, carbon dioxide and soot particles. Calculations are made to illustrate the relative impor ance of gas and soot emission under typical flame conditions.

rtson, R. M., Holmboe, E. L., Brown, F. B., Kirkland, J. T., Tullier, yton, R. B., Maritime Accidental Spill Risk Analysis Phase I: Method velopment and Planning, NTIS No. AD/761 362, January 1973.

This report develops a methodological approach and task plan for assessing alternative methods of reducing the potential risk cause by the spill of hazardous cargo as the result of vessel collisions and groundings. In addition to developing the overall study appro

rland, F. and Atkinson, G., The Interaction of Liquid Hydrocarbon With ter. U.S. Coast Guard, Office of Research and Development, NTIS No. AD/7 tober 1971.

This is an investigation of the phenomena reported in a Bureau of Mines report which studied the hazards of LNG. During the investigation, LNG was dropped onto a variety of liquid samples. Explosions did not occur when pure water was used as the sample, but water contaminated with n-hexane or toluence gave an explosion every time. Peak explosion pressures are given for a variety of experimental conditions.

ydon, A. G. and Wolfhard, H. G., Flames - Their Structure, Radiation and mperature. Chapman & Hall Ltd., London, 1960.

The book includes information concerning premixed flames, flow patterns and shapes, burning velocity; propagation, diffusion, stability, carbon in flames, radiation, temperature, ionization, combustion processes of rocket fuels, and recent progress on some flame problems.

rmeles, A. E., "A New Model for LNG Tank Rollover." Paper presented at t yogenics Engineering Conference, Kingston, Ontario, July 1975.

A dynamic model is presented which can give very accurate rollover predictions and is a potentially powerful tool in rollover prevention strategies. The excellent agreement between the predictions of the model and observations for the La Spezia rollover indicate that the model is valid. Uncertainties in the model transport coefficients indicate that further validation of the model would be desirable. The model has been computerized.

rmeles, A. E., "Forced Plumes and Mixing of Liquids in Tanks." Journal Fluid Mechanics. 71:601-623, 1975.

A mathematical model for the mixing of two miscible liquids of different density is presented, from which the tank stratification can be computed.

rmeles, A. E. and Drake, E. M., "Gravity Spreading and Atmospheric Disper on of LNG Vapor Clouds," Proceedings of the Fourth International Symposiu Transport of Hazardous Cargoes by Sea and Inland Waterway. Jacksonville tober 26-30, 1975, NTIS No. AD/A-023 505, pp 519-539, October 1975.

The paper presents methods for estimating the extent and location of flammable vapors as a function of spill and weather conditions, assuming that ignition does not occur. Models allow the width of the

ibson, G. H., "Consider Safety, Reliability, Cost in Selecting Type of
torage." Oil and Gas Journal, pp 65-69, February 8, 1971.

Several types of LNG storage are compared with respect to safety and cost.

ideon, D. N. and Putnam, A. A., "Dispersion Hazard from Spills of LNG
and and on Water." Cryogenics. 17, January 1977.

This report analyzes the pertinent published data on dispersion of vapors from LNG spills on land and water. Correlation of these da is based on the commonly used relationships from dispersion theory The report has emphasized peak concentration rather than average c 'maximum average' concentrations and for instantaneous spills. Th peak concentrations of major interest to safety, are related to th peak vaporization rates.

deon, D. N., Putnam, A. A. and Duffy, A. R., Comparison of Dispersion
IG Spills Over Land and Water. Report to the American Gas Association
ttelle Columbus Laboratories, Project IS-3-7, A.G.A. Catalog No. M198
eptember 4, 1974.

The report discusses dispersion variables, spill characteristics c water, a description of LNG programs, and provides comparisons of dispersion data.

deon, D. N., Putnam, A. A. and Duffy, A. R., "Safety Aspects of LNG S
Land." Advances in Cryogenic Engineering. 21. Paper presented at
yogenic Engineering Conference held at Queen's University, Kingston,
tario, July 22-25, 1975.

The paper provides information concerning experimental spills of L Instrumentation and procedures, the dispersion hazard, the radiati hazard, and fire control and vapor suppression are discussed.

fford, F. A., Jr., "Use of Routine Meteorological Observations for Es
ting Atmospheric Dispersion." Nuclear Safety. 2(4):47-51, June 1961

The article considers vertical dispersion of a cloud or plume and gives estimates of the lateral spread as well as wind speed and direction.

ldfeder, L. B., "Control Valves for LNG Facilities," Pipeline and Ga
urnal. pp 58-74, January 1972.

The types, applications and materials of construction of control valves for LNG are reviewed.

Goodwin, R. D. The Thermophysical Properties of Methane, from 90 to 500 at Pressures to 700 Bar. NBS Tech. Note 653, 1974.

An extensive tabulation of the thermophysical property data for Methane is presented. The temperatures covered range from 90 to 500 K and the pressure up to 700 bars.

Griffis, K. A. and Smith, K. A., "Convection Patterns in Stratified LNG Tanks - Cells Due to Lateral Heating." Paper presented at the 3rd Conf on Natural Gas Research and Technology, Dallas, TX, March 6-8, 1974.

The paper treats the subject of layer formation due to a uniform lateral heat flux, such as exists at an LNG tank wall. Experimentally, a water sugar system has been used to model the methane-higher hydrocarbon system. Preliminary results indicate that convective layers will be relatively thin for cases which are germ to LNG storage.

Guise, A. B., "How to Fight Natural Gas Fires." Hydrocarbon Processing 54:76-79, August 1975.

The following recommendations are made for coping with natural gas fires: 1) assume all fires to be impinging, 2) use potassium bicarbonate-base dry chemical, 3) use multipurpose dry chemical where water is not available, 4) use high velocity concentrated streams, and 5) use protective clothing and face shields.

Hall, A. R., "Pool Burning." Oxidation and Combustion Reviews. 6:169- Elsevier Scientific Publishing Company. 1973.

This review of literature includes: influence on the burning characteristics; temperature distribution in the liquid and the phenomena of hot zone formation and boilover; prevailing concepts of heat transfer from the flame to the liquid; effect of water as a dispersed phase, and as a substrate, on burning.

Hall, D. J., Barrett, C. F. and Ralph, M. O., Experiments on a Model of Escape of Heavy Gas. LR 217 (AP), Warren Spring Laboratory. Departmen Industry, Hertfordshire, United Kingdom, 1976.

The report describes model experiments on a release of a heavy explosive gas, propane or butane, into the atmosphere at ground level. Both long and short term released are considered and the validity of the model is discussed. A method of extrapolating the experimental results to full scale is provided.

Hankel, C. C., LaFare, I. V. and Litzinger, L. F., "Purging LNG Tanks
Out of Service Considerations and Experience." Paper presented to the
Transmission Conference, Minneapolis, Minnesota, May 6-8, 1974.

This paper discusses detailed procedures used by Chicago Bridge & Iron for purging LNG tanks into and out of service.

Harsha, P. T., LNG Safety Program Topical Report: Dispersion Modeling
Report RDA-TR-1100-003, by R&D Associates for the American Gas
Association, July 1976.

A variety of techniques exist for near-field LNG dispersion pheno. Gaussian plume models are inappropriate; hydrostatic models are appropriate; three-dimensional numerical models have been demonst a general LNG vapor dispersion model should incorporate sophistic state-of-the-art turbulence models.

Hashemi, H. T. and Wesson, H. R., "Cut LNG Storage Costs." Hydrocarbo
Processing. pp 117-120, August 1971.

Better, more precise designs can be made using a new mathematical model which more closely predicts actual boil-off rates. LNG los and storage costs are reduced.

Havens, J. A., Predictability of LNG Vapor Dispersion From Catastrophi
Spills Onto Water: An Assessment. Report prepared by the University
Arkansas for the Cargo and Hazardous Materials Division, Office of Mer
Marine Safety, U.S. Coast Guard, April 1977.

The author has reviewed various mathematical models and the methodology described by SAI and believes that such techniques hold the most promise for accurate prediction of vapor dispersion from catastrophic spills on water. A program designed to evaluat the accuracy of the SAI model or other models should now be considered high priority.

Heat Transfer at the Air-Ground Interface With Special Reference to Ai
Pavements. Report Prepared by the Massachusetts Institute of Technolog
ment of Civil and Sanitary Engineering, Soil Engineering Division, Tec
Report No. 63, January 1961.

The variables which affect the transfer of heat at the air-earth interface were studied as a part of an investigation to improve techniques for predicting subsurface temperatures. The investigation demonstrates that certain readily obtainable measurements may be utilized to predict the amounts of heat flow at the ground surface due to various atmospheric phenomena.

Heat Transfer in Fires: Thermophysics, Social Aspects, Economic Impact
Perry L. Blackshear, Ed, John Wiley & Sons, 1974.

The book, in five parts, considers social and economic aspects of fires; geometric parameters for classifying full-scale fires; heat and mass transfer in gaseous and condensed phases; radiative heat transfer associated with fire problems, and radiative transfer parameters.

Henry, R. E., Gabor, J. D., Winsch, I. O., Spleha, E. A. et al., "Large Vapor Explosions," Argonne National Laboratory, Argonne, IL. Paper presented at the Fast Reactor Safety Meeting, Beverly Hills, CA, April 1974.

Experimental results with Freon-22 and water show that the interfa temperature homogeneous nucleation model accurately predicts the necessary temperature conditions for the onset of large scale vapo explosions. Test results for many different contact modes reveale that the magnitudes of explosions were highly dependent upon conta mode.

Hertzberg, M., "The Theory of Free Ambient Fire. The Convectively Mixe Combustion of Fuel Reservoirs." Combustion and Flame. 21:195-209, 197

The theory of fuel-reservoir fires is extended and amplified into a quantitative formulation that includes all the significant physi processes: mass diffusion, heat conduction, convective mixing, convective heat transport, and radiative heat transport. The predictions are compared with the data for 3 fuels (gasoline, liquid hydrogen, and methanol), and the comparison gives reasonable agreement.

Hertzberg, M., Cashdollar, K., Litton, C. and Kansa, E., "The Diffusion in Free Convection. Buoyancy-Induced Flows, Oscillations, Radiative Ba and Large-Scale Limiting Rates." Paper presented at the Central States Combustion Institute Meeting on Fluid Mechanics of Combustion Processes Cleveland, OH, March 29-30, 1977.

Early studies of flame oscillations are reviewed and new data are presented for the fundamental infrared flicker frequencies of meth nol pool flames and other diffusion flames. Measured frequencies decrease monotonically with increasing size, in good agreement with independent data obtained photographically and acoustically.

eskestad, G. Kung, H. C. and Todtenkopf, N. F., "Air Entrainment into
rays and Spray Curtains." ASME Winter Annual Meeting, New York, New
976.

Theoretically derived volumes of entrained air were found to agree with experimental values to within 17%. While no explicit referen is made to LNG, the results are sufficiently general to apply to t vapor stage of an LNG spill.

ehne, V. O. and Luce, R. G., "The Effect of Velocity, Temperature, an
lecular Weight on Flammability Limits in Wind-Blown Jets of Hydrocarb
ses." Proceedings, Division of Refining, API, 50:1057-1081, 1970.

Various diameter jets of methane, ethane, butane, and heptane gas were directed perpendicular to the wind stream in a wind tunnel. Measurements were made to define the flammable zone caused by the jet-wind interaction. The application of the test results to practical process plant vent spacing to minimize hazards during windy atmospheric conditions is illustrated.

ttel, H. C. and Sarofim, A. F., Radiative Transfer. McGraw-Hill Book
mpany, Chapter 6. 1967.

Chapter 6 deals with gas emissivities and absorptivities.

ult, D. P., "The Fire Hazard of LNG Spilled on Waters", Proceedings o
portation and Terminal Safety. NTIS No. AD-754326, Boston, MA, June
72.

The paper considers the rate of evaporation of LNG spilled on wate the negatively buoyant plume, heat transfer to the plume, the buoyant puff, and concludes that there is no single rule whereby the fire hazard of an LNG spill may be estimated.

mbert-Basset, R. and Montet, A., "Dispersion dans l'Atmosphere d'un N
zeux Forme par Epondage de G.N.L. sur le Sol." Paper presented at th
ird International Conference on LNG, September 1972.

An experimental study conducted by GAZ de FRANCE at the test station of NANTES is described. To investigate the hazards occurring from spillage, measurements of evaporation rates of LNG on various soils were made. In addition, measurements were made of the extent that clouds generated from spillage in diked areas up to 200 m^2. A mathematical model was utilized in the extensive study of the hazards problem.

The Japan Gas Association, A Study of Dispersion of Evaporated Gas and Ign of LNG Pool Resulted From Continuous Spillage of LNG Conducted During 197 April 1976.

LNG spill tests were conducted for continuous releases to determine the characteristics of evaporation, dispersion, and ignition of pool fires. Tests were concerned mainly with the vapor cloud dispersion and the resultant cloud dimensions and character.

Jaquette, D. L., Possibilities and Probabilities in Assessment of the Haza of the Importation of Liquefied Natural Gas. Rand Corporation. Study P- AD-A019353, 1975.

Currently prevailing assessment of the safety hazards of LNG spills is criticized. The unknowns of such spills are listed and the need for more definitive information is stressed.

Jeje, A. A. and Reid, R. C., "Boiling of Liquefied Hydrocarbons on Water, Paper presented at the Third Conference on Natural Gas Research and Techn Dallas, TX, March 1974, sponsored by the American Gas Association.

The cryogens studied were liquid nitrogen, methane, ethane, and seve typical LNG compositions. In general, boiling fluxes increased slightly as the initial water temperature was lowered and as more cryogen was spilled. For LNG mixtures, significant foaming resulted and it is also suspected that ice is rapidly formed and remelted by eddy circulation in the upper layer of water.

Jeje, A. A. and Reid, R. C., Transient Pool Boiling of Cryogenic Liquids Water.

Boiling rates of LNG and LPG on water are determined as function of water temperature and liquefied gas composition.

Jensen, D. E., and Jones, G. A., "Reaction Rate Coefficients for Flame Ca tions." Combustion and Flame; 34: 1-34, 1978.

Current functional forms for chemical reaction notes and correspondi uncertainty factors are presented.

Katz, D. L., "Superheat-Limit Explosions." Chemical Engineering Progress 68:68-69, May 1972.

The rapidity of this superheat-limit event as compared to nucleated bubble growth in a partially superheated liquid provides an explanation for vapor explosions discussed in the literature.

cz, D. L. and West, H. H., "LNG Shipping and Storage." Paper Presente
gineering Foundation Conference on Risk/Benefit Methodology and Applic
lomar, California, September 21-26, 1975.

This article gives an overview of the history and development of th LNG industry with emphasis on storage and shipping. Potential haza associated with LNG are discussed briefly.

cz, D. L. and Sliepcevich, C. M., "LNG/Water Explosions: Cause and Ef
lrocarbon Processing. 50:240-244, November 1971; also NTIS No. AD-775

The paper discusses the limit of superheat, the methane-water syste LNG mixtures, massive LNG spills, and considers other systems such liquid methane poured into pure pentane in the absence of water.

e, R. J. and Miller, J. A., "A Split-Operator, Finite Difference Solut
Axisymmetric, Laminar-Jet Diffusion Flames." AIAA Journal; 16(2),
oruary, 1978.

An economical numerical solution of a vertical diffusion flame is presented. The complete chemical kinetics of the problem are inclu Discussions of possible numerical treatment of the thermo-hydrodyna and the "stiff" chemical kinetics are presented. "Majorant" splitting (as opposed to ADI methods) and the Gear-Hindmarsh "stiff" equation methods are utilized in the paper.

e, R. J., The Computational Nature of Combustion Modeling, Sandia Labo
ies, SAND78-8245, Albuquerque, July, 1978.

The report presents a fundamental approach to computations for combustion systems. Specific problems and numerical algorithms are presented.

ley, C. S., Radiative Transfer Between Flame Burning Zone and Unburne
l EATR-4555, Edgewood Arsenal, Maryland, NTIS-AD-732-405, October, 19

An assessment of the complex role of radiative heat transfer in the interaction of fuel and flame is presented. The thermo-physical properties of the fuel are included in the analysis.

g, W. S., On the Fluid Mechanics and Heat Transfer of Liquefied Natur
lls. RAND Corp., P5396, 1975.

A new mathematical model for the interaction between LNG and water is proposed. However, no details are supplied on the analytical an numerical details for practical use of the model.

Kneebone, A. and Prew, L. R., "Shipboard Jettison Tests of LNG Onto the Paper presented at the Fourth International Conference on LNG, Session 5 Paper 5, 1974.

The first part of the paper describes the procedures and results of a series of jettison tests carried out on board ship and discusses the operational safety aspects of such discharges. The second part is concerned with the environmental hazards associated with the rel of large quantities of LNG to the sea in terms of the extent of vap cloud formed; its characteristics and rate of dispersal.

Kogarko, S. M., "Detonation of Methane-Air Mixtures and the Detonation L of Hydrocarbon-Air Mixtures in a Large Diameter Pipe." Soviet Physics. 1958.

A review is made of the Russian literature on methane-air detonatio The author describes his work using tubes with diameters up to 0.305 meter and lengths to 12.2 meters. Gas mixtures were initiate with 50/50 amatol explosive charges. The author concludes that the limits and the possibility of a detonation vary with the diameter.

Lee, R. H. C. and Happel, J., "Thermal Radiation and Methane Gas," I&EC mentals. 3:167-176, May 1964.

The infrared absorption of methane in three wavelength regions (2.3 3.31, and 7.65 microns) has been determined at various temperatures and optical depths. The semiempirical expressions for the bank absorption so obtained are used to calculate the total and band emissivities of methane from 0.01 to 2.0 ft-atm. and from 500° to 3750°R.

Lehto, D. L. and Larson, R. A., Long Range Propagation of Spherical Shoc waves From Explosions in Air. U.S. Naval Ordinance Laboratory, White Oa Maryland, Report Numbers NOLTR 69-88 and AD 698 121, July 22, 1969.

Hydrocode calculations for spherical shock propagation using the artificial-viscosity method are carried out to 0.2 psi overpressure for a nuclear explosion and for a TNT explosion. An ideal-gas integration from the literature is used to extend the results to 1.6 x 10^{-4} psi. Below 1.0 psi, 1 kiloton nuclear is equivalent to 0.7 kilotons of TNT.

Levine, A. D., Theoretical Models of LNG Dispersion Studies (Phase III - Safety Program), Part I: Modeling of LNG Spills. AGA Project IS 129-1, Technical Report TLN-1, October 17, 1975.

A series of theoretical models relating to the growth and evaporati of cryogenic pools is reviewed, and new ones added in order to allo for complete empirical correlation. Agreement with all experimenta results is quite good although the scaling law is somewhat questio Continuous spills are modeled using harmonic function analysis wit adequate results.

evine, A. D., Theoretical Models for LNG Dispersion Studies. Report o .G.A Project IS-129-1, 1975.

Progress reports survey basic relations of detonation phenomena used to emphasize the importance of kinetics and induction time for the initiation process. Current knowledge of explosives in open air gas mixtures suggest that induction time may be very important in correlating experiments with theory.

ewis, D. H., The Dispersion and Ignitability of LNG Vapor Clouds. .S. Thesis, Massachusetts Institute of Technology, June 1974.

The flammability of vapor clouds resulting from instantaneous spills of LNG is determined quantitatively using statistical methods. A new physical theory on the vapor dispersion process is presented and compared to available experimental data. Numerical predictions of distance to various flammability limits are presented graphically.

ind, C. D., Explosion Hazards Associated With Spills of Large Quantiti azardous Materials - Phase I. U.S. Coast Guard Report CG-D-30-75, TIS No. AD-A001242. October 1974.

This report documents the results of a program to quantify the explosion hazards associated with spills of material such as LNG, LPG, or ethylene. The results are: a phenomenological descriptio of a spill; an examination of the detonation properties of methane a qualitative theory of non-ideal explosions; a plan for Phase II of the study.

ind, C. D. and Strehlow, R. A., "Unconfined Vapor Cloud Explosion Stud TIS No. AD-A023505 presented at the Fourth International Symposium on ransport of Hazardous Cargoes by Sea and Inland Waterways, Jacksonvill ctober 26-30, 1975.

Five-meter radius hemispherical bag tests of ignition of 10% metha propane-air mixture were conducted. Results indicated that igniti of fuels in this amount does not produce a detonation or damaging pressure waves.

iquid Natural Gas, Characteristics and Burning Behavior. Conch Methan ervices, Ltd., Villers House, Strand/London, W.C. 2, England.

A synopsis of a comprehensive engineering report prepared for Conc Methane Services Ltd., based on large-scale field tests conducted Lake Charles, Louisiana, plus laboratory data from the Bureau of M

LNG Safety Program - Interim Final Report. (Draft) R&D Associa
RDA-TR-1100-006 to the American Gas Association, September 30,

This program represents a comprehensive LNG safety study a the following tasks: LNG spread and boiloff rates. subsca experiments performed in a wind tunnel, dispersion modelin ation and detonation studies, and a field test program def which represents a major focal point of all other tasks. is placed on scaling, instrumentation, and data analysis m

LNG Safety Program - Interim Report on Phase II Work. A.G.A. P
Report to the American Gas Association by Battelle Columbus Lab
July 1, 1974.

Models for dispersion and radiation were developed, which for 80-ft spills and will predict the hazard for spills in up to 400 to 500 ft dia. Experiments verified reduction o hazards by insulated dike floors and high dikes. Predicti given of downwind distances of travel of flammable vapors ation intensities on targets near fires on soil, and in lo to 500 ft in dia.

LNG Terminal Risk Assessment Study for Los Angeles. Report by
cations, Inc., for Western LNG Terminal Company, December 22, 1

Science Applications, Inc., concludes on the basis of this that LNG risks to populated areas near the Los Angeles Ha are extremely low. The physical characteristics of LNG, t of the facility and tankship and the planned operating ru for the low risk values.

LNG Wind Tunnel Simulation and Instrumentation Assessments. Re
105700-003, Draft by R&D Associates for the U.S. Energy Researc
Development Administration, April 1977.

Information is presented on LNG flame radiation, test site wind tunnel modeling, and test instrumentation.

Love, T. J., Hood, J. D., Shahrokhi, F. and Tsai, Y. W., "A Met
Prediction of Radiative Heat Transfer From Flames." ASME Publ
presented at the ASME-AIChE Heat Transfer Conference and Exhib
August 6-9, 1967.

This paper presents a method, based on the transport equa predict the radiative heat flux from methanol and acetone of arbitrary size and geometry. Predicted and measured va the radiative flux were compared for several larger flame found to be in good agreement for free-burning flames of and methanol.

Mackay, D. and Matsugu, R. S., "Evaporation Rates of Liquid Hydrocarb
Spills on Land and Water." The Canadian Journal of Chemical Engineer
51:434-439, August 1973.

Experiments on the evaporation of cumene, water and gasoline are described and the evaporation mass transfer coefficient correlat with the windspeed, liquid pool size and the vapour phase Schmid Number. Comparison of the correlation with flat plate mass tran correlations shows satisfactory agreement and suggests that turb transfer occurs, the rate being enhanced by liquid surface rough

Maezawa, M., Experiments on Fire Hazards of Liquefied Flammable Gases
Osaka Gas Company, Ltd., May 1973.

Part 1 discusses the fire properties of liquefied flammable gase Part II presents the results of an experiment in fire extinguish Part III is concerned with a dispersion experiment. Briefly, th flame temperature of each liquefied gas is 700 to 800°C comparec gasoline at 1100°C. LNG burning rates are much larger than gaso line. Radiation energy is also larger than gasoline.

Maher, J. B. and Van Gelder, L. R. "Rollover and Thermal Overfill in
Bottom LNG Tanks." Pipeline and Gas Journal. 199:46-48, September 1

Conclusions are that high venting incidents involve thermal over surface layer phenomena occurs in flat bottom LNG tanks filled through bottom with a liquid of saturation pressure greater than pressure capability of the tank; bottom filled tanks should prov venting over entire fill time consistent with degree of thermal overfill; if top layer is continually agitated during filling, thermal overfill will not occur.

Markstein, G. H., "Scaling of Radiative Characteristics of Turbulent
Flames." Paper presented at the 16th International Symposium on Comb
1977.

It is shown that radiative properties of gaseous-fuel turbulent diffusion flames can be scaled successfully over a fairly wide range of fuel flow rates. In addition, radiometric scans were found to provide quantitative information on flame length and diameters and their scaling properties. The work was part of a program to develop a generally applicable model of fire radiatic

Martinsen, W. E., S. P. Muhlenkamp, J. Olson, "Disperse LNG Vapors W
Hydrocarbon Processing, 56(7):261-266, July 1977.

This paper discusses the potential for enhancing LNG vapor cloud dispersion by water sprays into the cloud. Experiments showed increased mixing due mainly to mechanical turbulence induced by the watery sprays and a resultant decrease in the distance a vapor cloud spreads before reaching the lower flammability limi

1asliyah, J. H. and Steward, F. R., "Radiative Heat Transfer From a Turbu
)iffusion Buoyant Flame With Mixing Controlled Combustion." Combustion a
Flame. 13:613-625, 1969.

A mathematical model of a turbulent buoyant diffusion flame is postulated. The radiative interchange between the flame and a plane surrounding its base is determined. From this radiative distribution, it is possible to determine the radiative heat flux to the liquid fuel which is vaporizing to feed the flame. A graphical solution is presented which yields the rate of burning of a liquid fuel of given physical properties in a fixed diameter fuel source.

May, W. G. and McQueen, W., "Radiation From Large LNG Fires." Combustion
Science and Technology. 7(2):51-56, 1973.

Radiation from flames of burning LNG were measured in a burning pool contained in a trench. Burning rates over the range of 13,500 to 40,000 BBL/D of LNG were studied. Measured flux varied from 60 t 480 Btu/hr/ft^2 at ground level and 300 to 600 feet from the flame center and from elevated points. An inverse square law of radiatior versus distance held fairly well.

May, W. G., McQueen, W. and Whipp, R. H., "Dispersion of LNG Spills." Hy
carbon Processing. 52:105-109, May 1973.

The paper discusses data analysis of plume shape and plume dispersion characteristics. Correlations show that dispersion of LNG vapors can be predicted from observed facts and controlled conditions.

May, W. G., McQueen, W. and Whipp, R. H., "Spills of LNG on Water." Pape
presented at the American Gas Association Distribution Conference, Washir
DC, May 14, 1973.

The conclusions reached cover: effect of variables on flow rate; inequality of downwind flow rate and evaporation rate; effect of density on plume shape; dependence of plume density on air humidity; effect of plume heating; weather effects; predictions of downwind plume travel.

May, W. G., and Perumal, P. V. K., The Spreading and Evaporation of LNG c
Water. ASME paper 74 - WA/PID-15, 1974.

The paper proposes a semiempirical relationship for estimating the total evaporation from a LNG spill on water. Correlations are basec on LNG spread rate, maximum pool diameter and evaporation rate per unit area.

ellor, G. L. and Yamada, T., "A Hierarchy of Turbulence Closure Models lanetary Boundary Layers." Journal of the Atmospheric Sciences. p 1791-1806, October 1974.

Turbulence models centered on hypotheses by Rotta and Kolmogoroff are complex. In the present paper, we consider systematic simplifications based on the observation that parameters governing the degree of anisotropy are small. Discussion is focused on density stratified flow due to temperature.

iller, B., "Possibilities in Hydrate Storage of Natural Gas." Gas Age 7:37-40, May 1942.

The formation of methane and LNG hydrates was reviewed. Data concerning hydrate storage, properties and decomposition pressures were discussed. Refrigeration and heat requirements for hydrate storage and regeneration were also presented.

ITRE Corp., A Summary of Accidents Related to Non-Nuclear Energy. EPA 00/9-77-012, PB-271506, 1977.

This report is an executive summary of a more extensive EPA study on accidents, in non-nuclear energy. LNG accidents are covered rather briefly, since only a few accidents have occurred in this category.

odak, A. T., "Thermal Radiation From Pool Fires." Paper presented at tates Section, The Combustion Institute Meeting, La Jolla, CA, October 976.

This analysis computes: radiative energy fluxes to surfaces locate external to the fire in any arbitrary orientation; variations of radiative heat flux along the fuel surface; total radiative heat transfer from flames to fuel surface; forward radiative heat transfer from fire to virgin fuel bed external to the fire; angular dis bution of radiative flux emitted by the pool fire; total radiative power output of the fire.

ontoya-Lirola, C., "Manufacture of Gels, Especially Liquid Fuels, and ubsequent Reversible Liquefaction." Span. 362, 146 (to Gelsa S. A.), hem. Abstrac. 76:27001g.

LNG could be gelled by generating a mixture of 20 percent water containing 2.5% of a vegetable albuminoid, saponin or viscous resinous gum with 80% LNG.

orton, B. R., "Modeling Fire Plumes." Paper presented at the Tenth Inte
ational Symposium on Combustion, Cambridge, UK, August 17-21, 1964.

Theoretical treatments for turbulent diffusion flames and for the strongly heated regions of fire plumes in a still environment may be based on those developed for weakly buoyant plumes. A discussion is given of some of the modifications that are needed, and the effec of large variations in density on the plume dynamics are aspects of heat transfer by radiation are presented separately.

Iullen, F. et al., Thermal Radiation and Overpressures From Instantaneous LNG Release Into the Atmosphere - Phase II. Final Report by TRW Systems Group to A.G.A., Report No. 08072-9, A.G.A. Catalog No. M60015, May 1969.

This report considers the fluid mechanics and thermochemistry of thermal radiation; boil-off, LNG vapor/air mixture dispersion experiments, and blast of overpressure; dike design; and a discussion of the flame program and vapor cloud studies.

Iunson, R. and Clifton, R. A., "Natural Gas Storage with Zeolites." U.S. National Technical Information Service, PB Report 1971, No. 203892.

Zeolites were used as an adsorbent for methane. For instance, Calcium A zeolite would retain up to 5 weight percent methane an 72°F and 200 psia. The potential of zeolites for vehicular natural gas storage was discussed.

Murgai, M. P., "Radiative Transfer Effects in Natural Convection Above Fi Journal of Fluid Mechanics. 12(3):441-448, March 1962.

This paper describes the results of examining the influence of radiative heat transfer on turbulent natural convection above fires in an atmosphere of constant potential temperature, under both the 'opaque' and 'transparent' approxmations. It turns out that on the basis of the overall approximations introduced in this investigation the former case reduces to that of no radiative transfer.

Murgai, M. P. and Emmons, H. W., "Natural Convection Above Fires." Journ of Fluid Mechanics. 8:611-624, 1960.

The turbulent natural convection above fires in a dry calm atmospher with a constant lapse rate has been the subject of several recent investigations. The present paper presents solution curves from which the natural convection may be computed over a fire of arbitrar size in an atmosphere with arbitrary lapse-rate variation.

Murray, F. W., Atmospheric Dispersion of Vaporized Liquefied Natural
Corp. Rpt. P5360, AD-A010 940, 1975.

A sophisticated mathematical model for the dispersion of LNG clo is proposed. However, no details on the equations and on their numerical treatment are given.

Muscari, C. C., The Evolution of Liquid Natural Gas on Water. M. S.
MIT, 1974.

Governing equations are given for the simultaneous spread and evaporation (burning) of an LNG spill on water. Equation soluti determine the 1) maximum radial extent of the spill, 2) time dur tion of complete dissipation of spill volume, 3) graphics of spi volume versus time, evaporation rate versus time and spill thick versus distance (from origin of spill).

Nakanishi, E., and Reid, R. C., "Liquid Natural Gas-Water Reactions."
Chemical Engineering Progress. 67:36-41, December 1971.

This paper cites previous studies and discusses both quantitativ and qualitative experimental results. Consideration is given to water on cryogens, underwater release of cryogens, cryogens on i cryogen spills on water and on coated liquids. Finally, a tenta hypothesis is presented for the explosion phenomena.

Neary, R. M., "Safety in LNG Semi-Trailer Design." Paper presented t
Transmission Conference, Las Vegas, Nevada, May 3, 1976.

Included in this paper is a description of LNG semi-trailers and the various DOT regulations regarding them. Also included is a discussion of and a picture of an LNG trailer that was exposed t a fire as a result of an accident.

Nelson, W., "A New Theory to Explain Physical Explosions." Combustio
May 1973.

This paper summarizes some known facts about explosions, with em on physical explosions, describes a new explosion mechanism, and suggests current and future applications of the new theory to pr smelt-water explosions in kraft chemical recovery furnaces.

Nielson, H. J. and Tao, L. N., "The Fire Plume Above a Large Free-Bur
Fire." Paper presented at the Tenth International Symposium on Combu
Cambridge, U.K., August 17-21, 1964.

A model which describes the variation with altitude of the compo sition, temperature, and velocity of the gases within a plume ab a large free-burning fire is presented. This model is an extens of previous analysis of buoyant plumes which includes the effect

Nierman, A. J., "Transportation of Natural Gas as a Hydrate." U.S. Pate
3,975,167 (to Chevron Research Co.), U.S. Patent Office, 1976.

Transportation of LNG hydrate by submarine was described. This procedure required supplementary refrigeration, a hold or void in which natural gas can be hydrated, and a membrane pervious to gas and water within the hold. Provisions were suggested for in situ removal of hydrate heat of formation.

Office of Technology Assessment, Transportation of Liquefied Natural Gas
Congress of United States, Washington, DC.

A review of LNG transportation technology provided as support for Congress on Future Energy Legislation. The LNG import system is criticized; Public concerns are summarized; and laws, permit requir ments and pending legislation are examined.

"Offshore LNG Terminal Deemed Feasible." Marine Equipment News, pp. 6-7
Spring 1977.

This article discusses the potential of offshore receiving terminal and describes several generic types that could be used. There are currently no offshore terminals in operation or construction, howev due to onshore siting difficulties they are being given serious attention.

Opschoor, G., "Investigations into the Spreading and Evaporation of LNG on Water." Cryogenics. 17:629-633, 1977.

Analytical expressions for the spreading of LNG spills on open and confined areas of water have been derived. They agree with known available experimental data.

Ordin, Paul M., Bibliography on Liquefied Natural Gas (LNG) Safety. NAS
Technical Memorandum NASA TM X-73408, April 1976.

This bibliography contains citations concerned with the safety of LNG and liquid methane. The raw data for this report was a compute printout based on a keyword search strategy of descriptions in the cryogenic safety data bank dealing with LNG.

Otterman, B., "Analysis of Large LNG Spills on Water - Part 1: Liquid S
and Evaporation." Cryogenics. 15(8):445-460, August 1975.

The first part of this two-part review considers the theoretical ar experimental results obtained on liquid spread and evaporation of large LNG spills on water. Both instantaneous spills, in which the spill time is much smaller than the time for complete vaporization, and continuous spills are considered. Also, applications of the correlations are discussed.

Panofsky, H. A., "The Atmospheric Boundary Layer Below 150 Meters." Review of Fluid Mechanics. 6:147-177, 1974.

The article considers profiles and fluxes over homogeneous terra (surface layers, extension to the tower layer) and profiles over changing terrain (wind profiles, temperature characteristics, en budgets, horizontal velocity components, temperature and humidit spectra, cospectra, and boundary layer models).

Parent, J. D., "The Storage of Natural Gas as Hydrate." Institute of Technology Bulletin No. 1, 1948.

A very thorough review of the technical literature was presented This included phase diagrams, heats of reaction, equilibrium rat cooling requirements, and operating pressures.

Parker, R. O., "Calculating Thermal Radiation Hazards in Large Fires. Technology. 10(2):147-152, 1974.

The author has developed, and discusses here, a method for asses the thermal radiation hazards to objects from fires. A comparis the calculations to an actual fire experience seems to indicate the method is reasonably accurate, though somewhat conservative.

Parker, R. O., "Study of Downwind Vapor Travel From LNG Spills." Pap presented at the American Gas Association Distribution Conference, Ma

The problem can be treated as a heat transfer calculation at the earth-liquid interface yielding the input; a second heat transfe problem if there is no wind, or if there is wind, an atmospheric dispersion problem. The conclusion is that it is very unlikely that vapor concentrations of more than 1/2 the lower flammable l will exist 600 or more feet downwind of the lee dike.

Parker, R. O. and Spata, J. K., "Downwind Travel of Vapor From Large of Cryogenic Liquids." Paper presented at LNG-1 Conference, Chicago, 1968.

A method is developed for calculating vapor concentrations downw of large pools of cryogenic liquids. Vapor concentrations at an downwind position is found as a function of time, wind speed, an wind structure. Lateral and vertical dispersion coefficients ar determined using meteorological observations. Practical applications include hazard studies and air pollution estimates.

Pergament, H. S. and Fishburne, E. S., "Influence of Buoyancy on Turbulen Hydrogen/Air Diffusion Flames." Paper presented at the Central States Se Combustion Institute Meeting on Fluid Mechanics of Combustion Processes, Cleveland, OH, March 29-30, 1977.

The results show that: flame properties scale with nondimensional distance for Froude numbers (Fr) greater than about 10^6; buoyancy affects temperature decay rates downstream of the location of maximum temperature (after all the H_2 has burned); the predicted influence of Fr on buoyant flame lengths is consistent with the available data.

Petrash, D. A., Barber, J. R., Chambellan, R., and Englund, D. R., "Gelle Liquid Methane." NASA Spec. Publ. NASA SP-5103, Sel. Technol. Gas Ind.: 86-88. 1975.

Results of work toward use of LNG as fuel for supersonic aircraft was reported. The problem of "boiloff" due to decrease of pressure with altitude was eliminated by preparing LNG gels with water or methanol. LNG-methanol gel was recommended due to the total heat of combustion.

Pipkin, O. A. and Sliepcevich, C. M., "Effect of Wind on Buoyant Diffusio Flames." Industrial and Engineering Chemistry Fundamentals. 3:147-154,

Buoyant diffusion flames of natural gas were observed in wind tunnel experiments to determine the extent of bending by wind. A flame dra coefficient, C_f, is introduced in the flame momentum balance. A single straight-line correlation of In C_f(Re) versus In Re is obtair after extracting the influence of flame angle of tilt and applying an empirical correction to account for increasing flame roughness at larger diameters.

Porricelli, J. D., Keith, V. E. and Paramore, B., Recommended Qualificati of Liquefied Natural Gas Cargo Personnel, Volumes I, II and III, NTIS No. AD/A026 109, AD/A026 110, April 1976.

The report presents recommendations, based on task analysis, concerning training and other qualification requirements appropriate for personnel of liquefied natural gas (LNG) ships and barges.

The study was a pilot effort to demonstrate a method of determining qualifications for new technology ship occupations when there are few or no operating examples to study.

Porteous, W. M. and Blander, M., "Limits of Superheat and Explosive of Light Hydrocarbons, Halocarbons, and Hydrocarbon Mixtures." AIC 21:560-566, May 1975.

Thirteen light hydrocarbons and 4 light halocarbons were testc determine their limits of superheat at one atmosphere pressure a superheating column. Even with some variation in temperatur which a compound could be superheated before boiling explosive reduced limits T_L/T_C were always close to 0.88. Super heat li of binary hydrocarbon systems and tertiary mixtures were close mole fraction averages of the limits of the pure compounds.

Porteous, W. M. and Reid, R. C., "Light Hydrocarbon Vapor Explosion Chemical Engineering Progress. 73:83-89, May 1976.

This article includes information relating to spills on water propane, propylene, isobutane, binary mixtures containing etha pure alkanes and pure alkenes. Some explosive compositions an ranges for hydrocarbon spills are also given. Previous studie are cited and factors affecting violence of explosions are dis

Priestley, C. H. B., and Taylor, R. J., "On the Assessment of Surfa Flux and Evaporation Using Large-Scale Parameters." Monthly Weathe 100(2):81-92, February 1972.

Data from a number of saturated land sites and open water site the absence of advection suggest a widely applicable formula f the relationship between sensible and latent heat fluxes.

Putnam, A. A., "A Model Study of Wind-Blown Free-Burning Fires." P presented at the 10th Symposium on Combustion, The Combustion Insti 1965.

Specifically, the dimensionless flame height varied with the negative 1/4-power of the Froude number based on cross-wind velocity and undisturbed flame height, above a Froude number of 0.2. The horizontal extension of the flame, on the other hand, increased rapidly with increasing cross wind at first, and then less rapidly with the 1/6-power of the Froude number.

Putnam, A. A., "Area Fire Considered as a Perimeter-Line Fire." Co and Flame. 7:306-307, 1963.

The hypothesis that line fires and area fires are basically related was tested by examining available data on sources in a line and in a hexagonal pattern. A mathematical analysis is given to justify the hypothesis.

Putnam, A. A. and Grinberg, I. M., "Axial Temperature Variation in a Tu
Buoyancy-Controlled, Diffusion Flame." Combustion and Flame. 9(4):419
1965.

An analytical expression was formulated which correlated the temperature profile of a turbulent diffusion, buoyancy-controlled flame to fuel properties and flow conditions. The expression is valid in the region after combustion is completed, and is valid at higher temperature levels than previously used correlations which are accommodated as a limiting case.

Putnam, A. A. and Speich, C. F., "A Model Study of the Interaction of M
ple Turbulent Diffusion Flames." Paper presented at the 9th Internatio
Symposium on Combustion, 1963.

This research program has shown that a valid model for studies of mass fires can be produced using multiple jets of gaseous fuels. The basic requirement is that the fuel jets produce turbulent diffusion flames which are buoyancy controlled. A specific operating range where this requirement is met was found for this model.

Radiative Transfer in Multidimensional Systems of Non-Gray Molecular Ga
Effects on Combustion. Columbia University. A.G.A. Project on LNG Fir
Study. (See LNG 1976 Annual Report).

An analytical technique has been developed to treat band radiation from non-gray molecular gases. The technique has been simplified so that the frequency integrations can be performed with simple quadrature formulae. The simplified technique is being applied to multidimensional radiative transfer problems as well as problems involving combustion.

Raj, P. and Emmons, H. W., "On the Burning of a Large Flammable Vapor C
Paper presented at the Central States Section, Combustion Institute Mee
April 1975.

A theoretical analysis is presented to estimate the ground level width of a two-dimensional turbulent flame as a function of time for the burning of a large combustible vapor cloud in the atmosphe for a given turbulent flame speed. The base width of the flame is assumed to be controlled by the rate at which the vapor is fed int the combustion zone and the air entrainment rate.

Raj, P. and Kalelkar, A. S., Assessment Models in Support of the Hazard Assessment Handbook. A report by Arthur D. Little, Inc., to the Departm of Transportation, U.S. Coast Guard, Report Numbers CG-D-65-74, NTIS No. AD 776617, January 1974.

Analytical models are derived to describe the hazards caused by the accidental release of chemicals into the atmosphere or spills onto water. The models encompass a variety of physical phenomena that can occur such as dispersion of vapor in the atmosphere, dispersion of liquid in water, spreading on water, burning of a liquid pool, etc. Analyses include the modeling of the phenomenon and solution to equations.

Raj, P. and Kalelkar, A. S., "Fire Hazard Presented by a Spreading, Burn Pool of Liquefied Natural Gas on Water." Paper presented at the Western States Section, Combustion Institute Meeting, 1973.

A time-growth rate for an LNG spill on water is obtained and the fire duration, determined by complete evaporation time, is establis An effective flame height is established and the radiation field about the flame calculated. Based on thermal radiation flux and fire duration, safe separation distances from the LNG pool fire for people and combustible materials (wood) are determined.

Ramsdell, J. V., Jr., and Hinds, W. T., "Concentration Fluctuations and to-Mean Concentration Ratios in Plumes From a Ground-Level Continuous Po Source." Atmospheric Environment. 5:483-495, 1971.

Diffusion data were collected by 63 incremental samplers during fou short duration, continuous releases of ^{85}Kr. *Cumulative frequency distributions and the intensity of short-term concentrations are shown to be a function of the relative crosswind position within the mean plume. Peak-to-mean concentration ratios are shown as a function of relative crosswind position within the plume and the ratio of the durations of the mean and peak.*

Rasbach, D. J., Rogowski, A. W. and Stark, G. W. V., "Properties of Fires Liquids." Fuel, 35:94-107, 1956.

Alcohol, petrol, benzole and kerosene fires, burning freely in a vessel of 30 cm dia, have been studied. Measurements were made on the temperature, rate of burning and change in composition of the liquid, and on the dimensions, upward velocity, temperature and emissivity of the flames. It was estimated that with hydrocarbon liquid fires, heat transfer to the surface was mainly by radiation, but for the alcohol fire mainly by conduction.

ausch, A. A. and Levine, A. D., "Rapid Phase Transformations Caused by
hermodynamic Instability in Cryogens." Cryogenics. 13:224-229, April 19

Thermodynamic metastability and incipient stability are used to explain the cause of rapid phase transformations. When liquid cryogen comes into sudden contact with a warmer host liquid, it is heated and forms a thin layer of metastable, superheated liquid at the interface. A heat transfer and thermodynamic model is used to predict the host liquid temperature that will cause a shockwave for a given cryogen.

aynor, G. S., Michael, P., Brown, R. M. and SethuRaman, S., "A Research
rogram on Atmospheric Diffusion from an Oceanic Site," BNL 18924 presente
t the Symposium on Atmospheric Diffusion and Air Pollution, Santa Barbara
A, September 9-13, 1974.

Analyses of meteorological data collected in this program show that wind profiles measured on the beach are representative of those over the ocean during onshore flows. Data obtained from tracer releases show that diffusion over the sea differs appreciably from that over land at the same time and is largely determined by the air-water temperature difference.

aynor, G. S., Michael, P., Brown, R. M, and SethuRaman, S., Studies of At
heric Diffusion From a Near-Shore Oceanic Site. BNL 18997, Brookhaven
ational Laboratory, June 1974.

Preliminary results show that diffusion is governed primarily by water and air temperature differences. With colder water, low-level air is very stable and diffusion minimal but water warmer than the air induces vigorous diffusion.

eid, R. C., "Superheated Liquids." American Scientists. 64:146-156,
arch - April, 1976.

The article cites numerous studies concerning superheated liquids and indicates that significant evidence suggests that superheated liquids are a trigger leading to the extensive fragmentation that may well set off large vapor explosions.

eid, R. C. and Smith, K. A., Boil-Off Rate of Liquid Nitrogen and Liquid
ethane on Insulated Concrete. Interim Report from MIT LNG Research Cent
o A.G.A., December 1975.

Experiments were conducted to measure the boil-off rate of both liquid nitrogen and liquid methane on insulation concrete. Results are fragmentary but do allow approximations of the rate of vapor generation that could result from spills of cryogens on typical insulating concretes.

eid, R. C., and Wang, R., The Boiling Rates of LNG on Typical Dike Flo
aterials. Cryogenics 18(3):401-404, 1978.

The insulating qualities for various types of floor materials for LNG dike storage compounds have been determined in LNG boiling tes Their numerical values are tabulated.

eisler, R. E., Ethridge, N. H., LeFevre, D. P. and Giglio-Tos, L., Air
last Measurements From the Detonation of an Explosive Gas Contained in
emispherical Balloon (Operation Distant Plain, Event 2a). U.S. Army
berdeen Research and Development Center, Ballistic Research Laborator
berdeen Proving Ground, Maryland, Report Numbers BRL MR 2108 and AD 73
uly 1971.

Air blast was measured from the detonation of a mixture of oxygen and propane equivalent to 20 tons of TNT in a hemispherical balloo anchored to the ground surface. Comparisons made of overpressure waveshape and impulse as a function of shock overpressure show an equivalent yield of 20 tons or larger and a dynamic pressure impul about 60 percent larger than for a corresponding 20 ton TNT charge

hoads, R. E. and Johnson, J. F., "Risk in Transporting Materials for V
nergy Industries." Nuclear Safety. 19(2):135-149, March-April 1978.

A risk assessment model is presented to assess the comparative safety of various energy systems in relation to other natural or man-related risks. Examples from assessments using the analysis technique are also presented along with future assessment plans. This paper encourages risk sensitivity studies and risk comparisons to provide a basis for decisions.

icou, F. P. and Spalding, D. B., "Measurements of Entrainment by Axisy
urbulent Jets." Journal of Fluid Mechanics. 11:21-32, 1961.

Measurements have allowed the deduction of an entrainment law relating mass flow rate, jet momentum, axial distance, and air density. When the injected gas burns in the jet the entrainment rate is up to 30% lower than when it does not.

ivard, W. C., Farmer, O. A., and Butler, T. D., RICE: A Computer Prog
ulticomponent Chemically Reactive Flows at All Speeds. LA-5812, March

A computer code capable of solving the thermal-hydrodynamics of chemically reactive flows is presented. A strong point of the cod is that it is not limited by sonic propagation constraints.

Rosenberg, S. D. and Vander Wall, E. M., "Gelled Cryogenic Liquids and Method of Making Same." U.S. 4,011,730 (to Aerojet-General Corp.), 1977.

LNG or methane hydrates were prepared by introducing finely divided solid water or methanol into the cryogenic liquid. Less than 2 weight percent decreased the solubility of nitrogen in LNG to nearly zero at -280°F.

Sarsten, J. A., "LNG Stratification and Rollover." Paper presented at th API Division of Refining, Philadelphia, PA, May 17, 1973.

This report covers an incident where LNG was stratified in an LNG storage tank during filling and how that stratification subsequently resulted in a rollover of the tank contents and the release of a large quantity of gas. A repetition will be positively prevented by the installation of a jet mixing nozzle that will thoroughly mix off loaded cargo with different composition initial tank heels.

Schuller, M. R., Murphy, J. C. and Glasser, K. F., "LNG Storage Tanks for politan Areas." Paper presented at the 4th International LNG Conference, Algeria, June 24-27, 1974.

This article describes in some detail the special design features of the 290,000 BBL storage tank built for Consolidated Edison of New York by the Pittsburg Des Moines Steel Company. The special design features, including a 9% Ni outer tank shell and a concrete berm wall around the outside of the tank, were used because of the heavily populated surrounding area and the proximity of the facility to LaGuardia Airport.

Science Applications, Inc., LNG Terminal Risk Assessment Study for Los Ar California. For Western LNG Terminal Company, Los Angeles, CA, SAI-75-61 1975.

SAI analyzed the potential risk of a proposed LNG import terminal in Los Angeles Harbor.

Sergeant, R. J. and Robinett, F. E., An Experimental Investigation of the Atmospheric Diffusion and Ignition of Boil Off Vapors Associated With a Spillage of Liquefied Natural Gas. Report by TRW Systems Group to the A. Report Number 08072-7, A.G.A. Catalog No. M19715, November 14, 1968.

Results of experimental spills of LNG into scaled earthen dikes are described. Emphasis of this phase of the program was directed toward qualitatively determining the path of the boil-off vapors, quantitatively measuring the gas/air mixture in the surrounding environment, and demonstrating the extent of the flammability with an ignition source. Correlation of the experimental data into empirical form is presented; radiation data were also obtained.

roka, S. and Bolan, R. J., "Safety Considerations in the Installation
LNG Tank." Cryogenics and Industrial Gases. pp 22-27, September/Oct
70.

Design codes and standards for LNG storage tanks are detailed. Diagrams showing instrumentation for a typical tank are included.

aheen, E. I., and Vora, M. K., "Worldwide LNG Survey Cites Existing, P
ojects," Oil and Gas Journal. pp 59-71, June 20, 1977.

This article discusses the various types of LNG facilities and brie describes several existing facilities. A list of all the LNG facilities worldwide is included.

ell Internationale Research, "Transportation of Liquefied Natural Gas.
th. Appl. 6,506,843, 1966. Chem. Abstr. 66:97298b.

An aqueous isopentane emulsion was used as a recyclable thermal carrier for heating or cooling LNG. A solid phase, such as silica-gel, was also suggested.

ultz, F. D., "Safety at an LNG Peakshaving Facility." Presented at th
ME Winter Meeting, New York, NY, November 17-22, 1974.

Design and operation of the many safety related aspects of Long Island Lighting Company's Holbrook LNG plant is described. Such features include gas detectors, fire protection and vapor dispersio systems, and the emergency shutdown systems.

manek, J. and Pick, P., "Hydrates of Natural Gas." Plyn. 53:167-9,
ne 1973.

Crystallographic data was presented concerning the unit cell and crystal dimensions. In natural gas, up to seven components can participate in mixed hydrate formation. Phase diagrams for severa of the mixtures were shown.

mmons, John A., Risk Assessment of Storage and Transport of Liquefied
tural Gas and LP-Gas. Science Applications, Inc., November 25, 1974.

A method for assessing the societal risk of transporting LPG and LNG is described. From an estimated 52 significant accidents per year with LPG tank trucks at the present truck-associated transportation rate of 20 billion gallons of LPG per year, a fatality rate of 1.2 per year is calculated. For the projected 1980 importa tion of 33 billion gallons by tanker ship, a fatality rate of 0.4 per year is calculated.

Sindt, C. F. and Ludtke, P. R., "Characteristics of Slush and Bo
and Methane Mixtures." Proceedings of 13th Int. Congr. of the In
Refrigeration, pp. 315-320, 1971.

*Experiments were performed to determine the boiling behavio
methane and methane mixtures and also of the slush which is
when vacuum pumping the ullage over the mixture.*

Singer, I. A., "The Relationship Between Peak and Mean Concentra
Journal of the Air Pollution Control Association. 11:336-341, J

*A method of predicting average concentrations has been pres
It has been shown that the simplified normal bivariate dist
describing the average concentration pattern is composed of
short-term periodic distributions which may differ from it
cantly. A descriptive, empirical method has been described*

Singer, I. A. and Smith, M. E., "Atmospheric Dispersion of Brook
Laboratory." Air and Water Pollution - An International Journal
1966.

*A variety of data relating to atmospheric dispersion has be
obtained at the Brookhaven Laboratory site and its environs*

*Concentration measurements were made at distances ranging f
10 m to 60 km. Dispersion patterns developed are discussed
detail and values of the parameters appropriate for various
theoretical treatments are summarized.*

Slade, D. H., "Atmospheric Dispersion Over Chesapeake Bay." Mor
Review. pp 217-224, June 1962.

*It was found that, after the air had traveled for about 7 m
over the water, its direction fluctuations were always less
they had been before reaching the water. The wind speed us
increased as the air crossed the water. The ratio of overl
overwater dispersive capacity varied from less than 5:1, fo
from below, to greater than 35:1 for cooling from below.*

Slawson, P. R. and Csanady, G. T., "The Effect of Atmospheric Co
Plume Rise." Journal of Fluid Mechanics. 47:33-49, 1971.

*The buoyant rise of chimney plumes is discussed for relati
large distances from the source, where atmospheric turbule
the dominant cause of mixing (rather than turbulence due to
plume's own upward motion). A simple theory is developed w
shows a number of different shapes plumes can have under d
atmospheric conditions (particularly in an unstable enviro*

an, E., Dendy, Khoury, F. M., and Kobayashi, R., "Water Content of Met in Equilibrium with Hydrates." Ind. Eng. Chem. Fundam. 15:318-23, il 1976.

Experimental measurements of water content of methane gas in equilibrium with hydrate were presented at 1000 and 1500 psia for temperatures greater than -10°F. The differences between methane and natural gas hydrates were stressed.

ch, K. A., Lewis, J. P., Randall, G. A. and Meldon, J. H., "Mixing and lover in LNG Tanks." Paper presented at the Cryogenic Engineering Con ence, Atlanta, GA, August 8, 1973.

Criteria and data are presented for deciding whether a specific LNG installation need have both top and bottom fill capacity. In genera a large facility will benefit from such capability if it is to recei a variety of LNG compositions from a variety of ships. It is furthe shown that the top fill device requires surprisingly careful design in order to assure good mixing at the free surface.

ch, K. A. and Reid, R. C., Boiling of LNG on Dike Floor Materials. M. Research Center, Cambridge, MA. 1976 Annual Report, Task VI, to the rican Gas Association BR 87-6, January 1977.

The rate of vaporization of LNG spilled on a number of substrates was measured experimentally. Included in the materials tested: insulated concrete of two densities, soil, sand, pebbles, wet and dry polyurethane. In all cases, the early rate of vaporization could be well correlated with simple, one-dimensional conduction heat transfer.

ch, K. A. and Reid, R. C. Electrostatics and its Hazards in Petroleum istry and LNG Systems. 1976 Annual Report, Task V, to the American Ga ociation BR 87-6, January 1977.

The paper discusses streaming potentials and sedimentation potential in relation to static charge generation as a consequence of hydro-carbon flow through pipes.

ch, K. A. and Reid, R. C., The Effect of Composition on the Boiling of on Water. 1976 Annual Report, Task IV, to the American Gas Associati 87-6, January 1977.

The results obtained thus far with binary and ternary mixtures indicate that a preferential evaporation of methane does indeed take place, followed by the preferential evaporation of the next more volatile component ethane. Propane is the last component to evaporate. Although a preferential evaporation takes place, the vapors are a mixture very rich in the volatile component but a mixture after all.

Airborne Effluents. Published by the American Society of Mechanical Eng
May 1968.

The guide discusses meteorological fundamentals, airborne effluents stack height, dispersion and deposition, data sources and experimen methods, and gives calculation methods and examples.

Spangler, C. V., "Storing Gases." U.S. 2,663,626 (to J. F. Pritchard an Co.), 1953.

Natural gas was cooled to slightly above its boiling point and adsorbed on activated carbon or silica gel. Release of adsorbed gas was achieved by contacting heated natural gas with the solid support.

Srinivason, K., et al., "Effect of Floating Insulation of Free Surface o Cryogenic Liquids in Open Containers." 6th Internat. Cryog. Eng. Conf., pp. 258-262, IPC Science and Technology Press Ltd., Guilford, England, 1

The effect of floating insulation materials on the evaporation rate of cryogenic liquids is investigated. Normally, this rate can be reduced by up to 25%.

Stanfill, I.C., "Startup Experiences and Special Features at Memphis LNG Presented at the First LNG International Conference, Chicago, IL, April 1968.

This paper describes four major and several minor equipment malfunctions which occurred during startup and the first six months of operation at the Memphis LNG plant. Several process flow diagrams for the Memphis plant are included.

Steward, F. R., "Linear Flame Heights for Various Fuels." Combustion ar Flame. 8(3):171-178, September 1964.

The flame heights of linear diffusion flames for several different fuels have been correlated with a single parameter derived from a model assuming mixing controlled combustion. The assumptions involved are stated clearly.

Steward, F. R., "Prediction of the Height of Turbulent Diffusion Buoyant Flames." Combustion Science and Technology. 2:203-212, 1970.

A mathematical model of a turbulent diffusion buoyant flame based c a number of simplifying assumptions is presented. It was found tha the height at which 400% excess air has been entrained corresponds the visible flame height according to data taken in our laboratory well as that presented by a number of other workers.

presented at the 14th Symposium on Combustion, The Combustion Institu
Pittsburgh, PA, 1973.

The author summarizes the history of accidental vapor cloud explosions, reviews the work that has been done to understand the dispersion, ignition, propagation and blast effects produced then points out areas for future investigation.

Strehlow, R. A. et al., "On the Measurement of Energy Release Rates i
Cloud Explosions." Combustion Science and Technology. 6:307-312, 19

The method is based on the finite amplitude isentropic acoustics of a centered spherical wave and involves the reduction of data from 3 pressure gauges which are measuring the explosion. The method of characteristics is used to back calculate to an effect spherical piston which replaces the explosion so energy release rates of the explosion can be calculated.

Study of LNG Safety - Parts I and II. Tokyo Gas Company Ltd., Centra
oratory, February 1971.

This two-part study presents experimental results on LNG evapora combustion and dispersion characteristics in a dike, and on LNG evaporation, ice formation, and LNG dispersion on water.

Sunvala, P. D., "Dynamics of the Buoyant Diffusion Flame." Journal o
Institute of Fuel. 40:492-497, 1967.

A new theoretical treatment of the axial velocity growth and mas concentration decay in a buoyant diffusion flame is presented. has been found that for the flame lengths of burning of various fuel gases, organic liquids as well as fuel oils, the one-fifth power index for the Froude Number holds good. However, for the flame lengths of burning firewood in cribs, the two-fifths power index for the Froude Number is suggested.

Tanker Structural Analysis for Minor Collisions. U.S. Coast Guard Re
CG-D-72-76, NTIS No. AD/AO 31031, December 1975.

This report describes the work accomplished during the course of the project of the Evaluation of Tanker Structure in Collision. The intent of the report is to present the investigations perfor in evaluating the phenomena that contribute to the ability of a longitudinally framed ship, particularly a tanker, to withstand minor collision. A minor collision is one in which the cargo ta remain intact. The ability to withstand a minor collision is quantized by the total energy that can be absorbed during the collision.

Tarifa, C. S., Del Notario, P. P. and Valdes, C. F., Open Fires. Final Report, U.S. Department of Agriculture, Forest Service, Grant FG-SP-114 and 146, May 1967.

An experimental study was made of some basic laws of open fires by utilizing the pool fire techniques. Data were obtained for burnin rates, energy balances and flame characteristics, including the influence of fuel type, vessel size and vessel configuration.

Taylor, P. B. and Foster, P. J., "Some Gray Gas Weighting Coefficients CO_2-H_2O Soot Mixtures." International Journal of Heat Mass Transfer. 1332, 1975.

Two tables are provided which give 1) the values of constants whic specify weighting factors for various soot concentrations applicab in the temperature range 1400 to 2400°K and 2) values of constants which specify the gray gas absorption coefficient applicable in th 1200 to 2400°K temperature range.

Thermal Radiation and Overpressure from Instantaneous LNG Release into Atmosphere. Report by TRW Systems Group to A.G.A., TRW Report No. 080 April 26, 1968.

The report conclusions express belief that 1) a stoichiometric mixture of natural gas and air at atmospheric pressure will not detonate with a charge of high energy explosive equivalent to 625 grams of TNT; 2) the parameters of charge energy, mixture composition and confining wall geometry should be further investig

Thomas, P. H., "The Size of Flames From Natural Fires." Paper presente the 9th International Symposium on Combustion, 1963.

Uncontrolled fires produce flames where the initial momentum of the fuel is low compared with the momentum by buoyancy. The heigh of such flames with wood as the fuel are examined and discussed in terms of both a dimensional analysis and the entrainment of air into the turbulent flame. Some recent experiments on the effects of wind on such flames are also reported.

Thomas, P. H., Baldwin, R. and Heselden, A. J. M., "Buoyant Diffusion Some Measurements of Air Entrainment, Heat Transfer, and Flame Merging Paper presented at the 10th International Symposium on Combustion, the Combustion Institute, 1965.

Thistledown has been used as a tracer to measure the flow of air toward ethyl alcohol and wood fires 91 cm in diameter, and a smal town gas fire. The measured mean axial temperature rise at the mean flame height was about 300° to 350°C for wood and alcohol and 500°C for town gas.

ner, D. B., Workbook of Atmospheric Dispersion Estimates. Public Hea
vice Publication No. 999-AP-26, 1969.

This workbook presents methods of practical application of the binormal continuous plume dispersion model to estimate concentrations of air pollutants. Estimates of dispersion are those of Pasquill as restated by Gifford. Emphasis is on the estimation of concentrations from continuous sources for sampling times up to 1 hour.

, A. E., Amoroso, L. A., and Sertir, R. H., "Safety and Reliability of
Facilities." Presented at the ASME Petroleum Mechanical Engineering
ssure Vessels and Piping Conference, New Orleans, LA, September 17-21,

The prime factors behind the fine operational safety and reliability record of LNG facilities are the early definition and understanding of the nature of LNG, the establishment and utilization of relevant codes, the casting and observation of pertinent quality assurance programs, and thorough training of plant operators. This paper discusses each of these factors in detail.

der Wall, E. M., "Investigation of the Suitability of Gelled Methane
Use in a Jet Engine." NAS 3-14305, NASA CR-72876, 1971.

Methanol gelled cryogenic methane was storable at -263°F for periods exceeding 100 hours with no significant gel structure degradation. The gel could be transferred through properly designed heat exchange at comparatively high flow rates (10 lb/hr) without clogging. Fuel consumption by jet engines was not excessive due to the gelant.

Horn, A. J. and Wilson, R., Liquefied Natural Gas: Safety Issues,
lic Concerns, and Decision Making. Energy and Environmental Policy Ce
ferson Physical Laboratory, Harvard University, Informal Report BNL 22
ember 1976.

The report provides background information on LNG and discusses safety issues, LNG facilities siting disputes, public concern for LNG facilities siting, LNG decision making, and gives recommendations concerning LNG terminal siting facilities.

ta, E. B. et al., Detonability of Some Natural Gas-Air Mixtures. Air
ament Laboratory, Elgin Air Force Base, Technical Report AFATL-TR-74-8
il 1974.

A bag test method to screen natural gas-air mixtures (5.2 to 12.5% by vol. natural gas) to determine detonability. At the 8.6 to 8.8% concentration level, erratic, uneven detonations were initiated and explosive charges ranged from 1001 to 1020 grams. Deflagration occurred at all other fuel concentrations. The detonations propagat the length of the bag, but a steady Chapman-Jouguet type wave front

roceedings of the First International Loss Prevention Symposium. The H
elft, The Netherlands, May 28-30, 1974. The Proceedings is Entitled Lo
revention and Safety Promotion in the Process Industries, C. H. Buschma
lsevier Scientific Publishing Company, 1974.

It is shown that the spreading of a heavy gas differs essentially from the spreading of a neutral gas. Horizontal spread is increase considerably by gravity effects, whereas vertical spread is limited Calculations are compared with experimental results.

arma, R. K., Murgai, M. P. and Ghildyal, C. D., "Radiative Transfer Eff n Natural Convection Above Fires - General Case." Proc. Roy. Soc., Lon .314, 1970.

The effect of radiation, on the overall dynamics of a hot plume above fires, has been considered. An approximate multidimensional transfer equation for heat radiation is derived from the Schwarzsch equation. The plume material is assumed to be grey and the outside atmosphere is considered calm and is, otherwise, in a state of arbitrary lapse rate variation.

/erma, S. B. and Cermak, J. E., "Mass Transfer From Aerodynamically Roug Surface." International Journal of Heat and Mass Transfer. 17:567-579,

Mass transfer rates were determined by directly measuring the actua volume of water evaporated from saturated wavy (sinusoidal) surface in micrometeorological wind tunnel. Simultaneous measurements of mean velocity, humidity and temperature distributions were made ove these saturated waves.

Nakeshima, H. and Takata, K., "On the Limit of Superheat." Journal of t Physical Society of Japan. 13(11):13-1403, November 1958.

A new method was devised in which small drops of a sample liquid are heated as they rise up in the nonsoluble heating liquid with a suitable temperature gradient upward. The limit of superheat was determined for saturated hydrocarbons and polymethylenes. The agreement between (Doring's) theory and experiment was satisfac

Nelker, J. R., Brown, L. E., Ice, J. N., Martinsen, W. E., and West, H. Fire Safety Aboard LNG Vessels. U.S. Coast Guard Report No. CG-D-94-76, NITC No. AD-A030619, January 1976.

This report presents results of an analytical examination of cargo spill and fire hazard potential associated with the marine handling of liquefied natural gas cargo. Principal emphasis was on cargo transfer operations at receiving terminals, and more specifically on the LNG tanker's cargo handling and hazard sensing and control equipment and operations.

the A.G.A. Operating Section Distribution Conference, 1969.

This paper concludes that: flammable mixtures from large spills will penetrate a long distance downwind; a major spill should be ignited as soon as possible; a high-expansion foam system offers the best protection by suppressing either LNG evaporation or the burning rate and present standards that specify separation distance irrespective of pool size are meaningless.

ker, J. R., Pipkin, O. A. and Sliepcevich, C. M., "The Effect of Wind mes." Fire Technology. 1(2):122-219, 1965.

A simplified and improved correlation for the drag coefficient of windblown natural gas flames is given. Experimental results leadin to the correlation were obtained in a low-speed wind tunnel specifi cally designed for such studies at the University of Oklahoma North Campus.

ker, J. R. and Sliepcevich, C. M., "Bending of Wind-Blown Flames From uid Pools." Fire Technology. 2, 1966.

The bending of a flame by wind influences the amount of heat transferred by radiation and convection, the fuel burning rate, and the flame spread rate. To what extent will a flame be bent by wind? The author presents correlations of data taken from liquid pool fires, which enable us to predict flame bending and trailing for large fires.

ker, J. R., West, H. H., Mento, M. A. and Ice, J. N., A Survey of the ectiveness of Control Methods for Fires in Some Hazardous Chemical goes, U.S. Coast Guard Report CG-D-64-76, NTIS No. AD/A026300, March

Assessment of fire safety of marine bulk chemical carriers was attempted. It is recommended that standard fire control test methods be developed together with standardized test data collecting and reporting methods and that large-scale fire tests be made on chemicals from different families to attempt to develop methods of correlation with small-scale test results. If a reliabl correlation can be developed, small-scale tests could be used in the future with more confidence to both predict behavior of chemical cargoes under fire conditions and to assess large fire extinguishing effectiveness.

st, H. H., Brown, L. E. and Welker, J. R., "Vapor Dispersion, Fire Cont
d Fire Extinguishment for LNG Spills." Proceedings of the Fourth Inter
tional Symposium on Transport of Hazardous Cargoes by Sea and Inland Wa
cksonville, FL, October 26-30, 1975. Report Number AD/A-023 505, pp 50
tober 1975.

Dry chemical fire extinguishment systems can provide rapid extinguishment of LNG fires. High expansion foam can reduce the radiant flux from LNG fires, provide protection for the surroundings until the fire burns out, and reduce the concentration of methane in the vapor cloud downwind from an LNG fire.

est, H. H., Brown, L. E. and Welker, J. R., "Vapor Dispersion Fire Contr
nd Fire Extinguishment for LNG Spills." The Combustion Institute, 1975
echnical Meeting. San Antonio, Texas, 1975.

The paper reports results on AGA tests of LNG evaporation and pool fire radiation reductions by foam application. Tests also demonstra flame extinguishment by dry chemicals if applied a short time after pool fire ignition.

ilcox, D. C., "Model for Fires With Low Initial Momentum and Nongray The
adiation." AIAA Journal. 13(3):381-386, March 1975.

A new ambient-air entrainment law accounts for rapid fluid acceleration from initially low velocity at a liquid pool, to higher velocit established under buoyant rise of the combustion products. Radial-radiation heat transfer is computed with the exact radiation transpo equation. Fire-model predictions fall within scatter of experimenta flame-height and spectral-radiation data for LNG fires.

ilcox, D. C., NonGray Thermal Radiation From a Flame Above a Pool of Lic
atural Gas. Report by TRW Systems to A.G.A., A.G.A. Catalog No. M19714,
ebruary 1971.

This report indicates that a) spectral distribution of the radiatior heat flux vector can be calculated, b) minimal data are required to extrapolate from small to large fires, c) an important scaling relationship may have been uncovered, and d) the flame model and associa ted computer program represent a solid foundation for investigation of radiation properties of a large LNG fire.

illiams, Forman A., Combustion Theory - The Fundamental Theory of Chemic
eacting Flow Systems. Addision-Wesley Publishing Company, Inc., 1965.

Chapter 2 discusses Rankine-Hugoniot relations and pages 25-27 the properties of the Hugoniot curve.

Wissmiller, I. L. and Mattocks, E. O., "How to Use LNG Safely." Pipe
Gas Journal, March, 1972.

This article provides a general description of LNG equipment and facilities and how they are designed and operated for safety.

Witte, L. C. and Cox, J. E., Nonchemical Explosive Interaction of LNG
Water. ASME Preprint 71-WA/HT-31, 1972.

When LNG contacts water, an explosive incident may occur due to extremely rapid production of LNG vapor as heat is transferred from the surrounding water. Pertinent literature is summarized on similar reported explosions when hot molten materials contact cool liquids. Fragmentation of the LNG is believed to be the triggering mechanism for explosive vapor formation. Recent resu of fragmentation research are presented.

Witte, L. C., Cox, J. E. and Bouvier, J. E., "The Vapor Explosion."
of Metals. 22:39-44, February 1970.

The article reviews the four theories of entrapment, violent boi shell theory, and Weber Number Effects. A common factor exists that when molten material is fragmented prior to liquid contact, explosion danger is lessened.

Witte, L. C., Vyas, T. J. and Gelabert, A. A., "Heat Transfer and Frag
tion During Molten-Metal/Water Interactions." Journal of Heat Transf
95:521-527, November 1973.

This study indicates strongly that fragmentation occurs when a sample is molten and fragmentation is a response to an external stimulus. Alternate causes of fragmentation are proposed and ar predicated upon the initial collapse of a vapor film around the molten metal.

Wood, B. D., Blackshear, P. L., Jr, and Eckert, E. R. G., "Mass Fire
An Experimental Study of the Heat Transfer to Liquid Fuel Burning Fro
Sand-filled Pan Burner." Combustion Science and Technology. 4:113-1
1971.

Heat flux data and the radiation heat flux data indicate that radiation contributes between 20 and 40 percent of the thermal l to the fuel surface for the methanol flame. For the acetone fla approximately 40 to 60 percent of the total heat flux is radiati during the two steady burning rate periods.

oolers, R. G., Marine Transportation of LNG and Related Products. Cornell
ime Press, Cambridge, MD, 1975.

This book describes aspects of marine transport of LNG including ship design, container design, control systems, and a description of hazards and LNG importation. The hazards section describes experiments performed by the Bureau of Mines to determine the effects of LNG spillage on water.

amazaki, D., Yokoyama, N, and Hino, M., "Storing and Transportation of
ydrocarbon Gases." Japan Kokai 73-92, 401 (to Mitsubishi Heavy Industrie
td.), 1973. Chem. Abstr. 80:85488q.

Natural gas was contacted with aqueous aliphatic amine solutions to obtain the hydrate. The hydrate product had a vapor pressure of 35 kg/cm^2 at 40°F.

ilmaz, B. S., Clarke, S. F. and Westwater, J. M., Heat Transfer From Wate
n Film Boiling to an Upper Layer of Paraffinic Hydrocarbon. ASME paper
6-HT-24, 1976.

Laboratory experiments have been performed to measure the flux from a layer of water in the state of film boiling to a superimposed layer of various types of hydrocarbons.

umoto, T., "Heat Transfer From Flame to Fuel Surface in Large Pool Fires.
ombustion and Flame. 17:108-110, 1971.

The study was made to obtain experimentally the ratio of radiation and convection transfers to total heat transfer from the flame to the fuel surface in the range where the burning rate has a constant value regardless of pan diameter.

uber, K., "LNG Facilities - Engineered Fire Protection Systems." Fire Te
ology. 12:41-48, 1976.

Dry chemical fire extinguishers used in conjunction with high expansion foam have been used successfully in tests to extinguish LNG spill fires.

Bailey, F. B., "Status of United States Codes and Regulations Affectin Based LNG Facilities." 1978 Operating Section Proceedings, American G Association, Montreal, Quebec, May, 1978.

This report summarizes current safety and non-safety regulations, and activities concerning regulations. NFPA59A versions and applications listed.

Bijl, P., Vet, P. N., Novel Approach Required for LNG Peakshaving Plan in the Netherlands. Oil and Gas Journal, pp. 81-85, November 28, 1977

This article describes a unique peakshaving facility which produces bo LNG and liquid nitrogen, LN_2. Because of the high N_2 content of the g in the Netherlands, a slightly modified expander liquefaction cycle wa designed which allowed separation of LN_2 from the LNG.

Bradley, D., Mitcheson, A., The Venting of Gaseous Explosions in Spher Vessels I, II. Combustion and Flame, 32:221-237, 1978.

The authors present various theoretical analyses of the pressure rise partially confined reactive systems. The results of these investigati are then compared with experimental data and recommendations are made proper venting procedures.

Brown, L. E., Martinsen, W. E., Muhlenkamp, S. P., Pucket, G. L. Smal Scale Tests on Control Methods for Some Liquefied Natural Gas Hazards. University Engineers Report UE-308-FR, AD-A 033522, 72 pp., 1976.

A detailed description is given on field tests to extinguish small sca LNG fires by dry chemical application. Water sprays proved to be effe in reducing radiant heating on exposed areas.

Chippet, S., and Gray, W. A., "The Size and Optical Property of Soot Particles." Combustion and Flame, 31:149-159, 1978.

This paper presents the results of an experimental investigation to determine the spectral transmissivity and size distribution of soot aggregates. Measured attenuation and light scattering were found to b in best agreement with theoretical results when the complex refractive index, $\overline{U}$, was taken to be 1.9-0.35i.

Chiu, Chen-Hwa, "Evaluate Separation for LNG Plants." Hydrocarbon Proc pp. 266-272, September, 1978.

Energy losses from various processes involved in separation of LNG com during liquefaction are discussed. Losses due to compression and liqu were cited to show areas for improvement in energy use.

Creighton, J. R., A Two Reaction Model of Methane Combustion
Numerical Calculations. September 28, 1977.

Inclusion of chemical kinetics in the computational schemes dimensional thermo-hydrodynamic codes (involving flame propa results in prohibitively expensive computational time. The this report attempts to develop a simplified flame propagati (of possible use in Langrangian-Eulerian hybrid codes) which acceptable values of flame velocity, temperature and pressur

Desgroseilliers, G. J. Radiation from Burning Hydrocarbon C
M.S. Thesis, MIT Department of Mechanical Engineers, p. 88,

Radiation test data from the combustion of methane, ethane a are reported. Tests are of small scale with the vapors init tained in soap bubbles. A newly-developed mathematical mode fairly well with the experimental results.

DiNapoli, R. N., "LNG Peakshaving Plants Require Careful Cos
Pipeline and Gas Journal, pp. 28-36, May, 1978.

The paper reports a dearth of data on the costs of LNG peaks construction probably due to the competitive nature of the L industry. Generalized costs for peakshaving and satellite f presented.

Drake, E. M., Geist, J. M., Smith, K. A. Prevent LNG "Rollo
carbon Process. 52:87-90, March, 1973.

"Rollover" is a sudden release of large amounts of vapor, wh when LNG is added to a storage tank already containing some composition. Even though not very dangerous, such events sh be avoided for reasons of safety.

Feirabend, C. E., "Design Considerations for LNG Production
Arctic Regions." 1978 Operating Section Proceedings, Americ
Association, Montreal, Quebec, May, 1978.

Operational and engineering design responses to extremes of and windspeed in arctic regions are considered.

Hall, D. J., Barrett, C. F. and Ralph, M. D. Experiments or
an Escape of Heavy Gas. Warren Spring Laboratory LR217(AP)
Hertfortshire, U.K., 1976.

The report describes wind tunnel experiments simulating rele heavy explosive gas, propane or butane, into the atmosphere level. Both long and short term releases are considered and of the model is discussed. A method of extrapolating the e results to full scale is provided.

Hardee, H. C., Lee, D. O., Benedick, W. B. Thermal Hazards from LNG Fireballs. Combustion Sci. and Techn. 17:189-197, 1978.

LNG fireballs can pose serious burn hazards in their vicinity. Third degree burns from a very large LNG fireball (several 10^7 kg) could occu out to several kilometers from its center.

Hashemi, H. T., Lott, J. L., Wesson, W. D. and Wesson, H. R. "Effect o Barometric Pressure Changes on Rate of Boiloff in a Storage Tank of Saturated Liquids." 1978 Operating Section Proceedings, American Gas Association, Montreal, Quebec, May, 1978.

An analytical model for prediction of boiloff variations due to atmosph pressure changes in atmospheric storage tanks is presented. LNG exampl are shown although the model can be applied to various other cryogenic gases.

Hindle, W. Arctic Islands LNG. Presented to the American Gas Associat Transmission Conference, Montreal, Quebec, May 8-10, 1978.

Trans Canada has begun the study and design of an LNG project which wou transport LNG from the high Arctic Islands to Quebec. The type of ship that would be used, an icebreaking LNG carrier, is described.

Jamison, L. R., "United States Codes and Regulations Affecting the Mari Aspects of LNG Movements." 1978 Operating Section Proceedings, America Gas Association, Montreal, Quebec, May, 1978.

This paper presents a collection of regulations which influence marine movement of LNG. Agencies regulating this transport are the U.S. Coast Guard, Intergovernmental Marine Consultative Organization, and the Repu of Liberia Bureau of Marine Affairs.

Katz, D. L., "LNG-Water Explosions." AD-775005, 1973.

The "limit of superheat" is identified as the cause of LNG-water explosions. However, theoretical support for this argumentation is mainly speculative.

Kaustinen, O. M., "Polar Gas Project." Presented to the American Gas Association Transmission Conference, Montreal, Quebec, May 8-10, 1978.

Some of the alternative methods of moving natural gas from Canada's Arctic Islands are discussed.

Lawrence, G. H., "Comments of the American Gas Association on Delegatio of Functions by the Secretary of Energy to the Administrator of the ERA and FERC." American Gas Association, November 15, 1978.

The American Gas Association requests revision of the delegation due to confusing and inconsistent language, a failure to correct jurisdictiona overlaps, and the increasing cost of regulations.

Tests have been conducted to investigate the burning behavior of LNG typ materials. No detonations have been observed in any of these tests.

Magnussen, B. F. and Hjertager, "On Mathematical Modeling of Turbulent Combustion with Special Emphasis on Soot Formation and Combustion." Presented at the 16th International Symposium on Combustion, pp. 719-729 1976.

This paper presents a mathematical model of turbulent diffusion and/or premixed flames. Methods for thermal radiation and soot formation predictions are also presented. Soot formation is analyzed as a two-ste process (nucleation site formation and soot particle formation). Therma radiation is evaluated using a two-flux equation.

Meroney, R. N., Neff, D. E. and Cermak, J. E., "Wind Tunnel Modeling of LNG Spills." 1978 Operating Section Proceedings, American Gas Associati Montreal, Quebec, May, 1978.

The author's report scales of spill conditions that may be successfully simulated in Colorado State University wind tunnels. Simulations of 1974 AGA LNG land spill experiments and uses of wind tunnels in experimental design are also discussed.

Miller, R. C. and Hiza, M. J., "Experimental Molar Volumes for Some LNG-Related Saturated Liquid Mixtures." Fluid Phase Equilibria, 2:49-57, 19

Saturated (orthobaric) liquid molar volumes are reported for some methan rich mixtures containing ethane, propane, isobutane, normal butane and nitrogen at temperatures between 100 and 115 K. These data were obtaine with a gas-expansion system calibrated against pure methane orthobaric liquid molar volumes. Comparisons are shown between the experimental molar volumes and the results of some recent calculational methods.

Murray, F. W., Jaquette, D. L. and King, W. S. Hazards Associated with the Importation of Liquefied Natural Gas. Rand Corp., June, 1976.

Four previous reports by Rand Corporation are summarized and updated in this most recent publication, which discloses probable causes of accidental spills of LNG, the hazards surrounding these spills, and methods of estimating the probabilities of major accidents. In assessing the risks associated with LNG transport and processing, it is concluded tha not enough evidence has been collected to comment on the safety of LNG or the ability to extrapolate results from past experience.

Nuclear Regulatory Commission, "Safety Evaluation by the Office of Nuc Reactor Regulation Regarding the Proximity of Cove Point LNG Facility: Baltimore Gas and Electric Company Calvert Cliffs Nuclear Power Plant Units Nos. 1 and 2." Docket Nos. 50-317 and 50-318, March 13, 1978.

An analysis is described which shows the effects of various hypothetic LNG accidents at Cove Point on the Calvert Cliffs Power Plant. Result indicated that no new operating restrictions or other limitations need to be placed on the plant to assure normal operations.

Parrish, W. R., Arvidson, J. M. and LaBrecque, J. F., "Evaluation of LNG Sampling Measurement Systems for Custody Transfer." 1978 Operatin Section Proceedings, American Gas Association, Montreal, Quebec, May, 1978.

A method for sampling moving LNG streams for composition and heating value is described. The main component of the technique and the main source of error is a gas chromatograph.

Parrish, W. R., Arvidson, J. M. and LaBrecque, J. F., "System is Accur Precise for LNG Sampling." Hydrocarbon Processing, April, 1978.

A three component system including a sampling probe, vaporizer, and ga analyzer is described which can be used to monitor heating value from moving streams of LNG. Detection error is derived mainly from error i the gas analyzer.

Parrish, W. R., Brennen, J. A. and Siegwarth, J. D., "LNG Custody Tran Research at the National Bureau of Standards." 1978 Operating Sectior Proceedings, American Gas Association, Montreal, Quebec, May, 1978.

This paper presents a summary of research on determining the thermo-physical properties of LNG components, on flowmeters, and on LNG sampling and composition measurements.

Reid, R. C., Superheated Liquids. American Scientist, 64(2):146-156,

The principle of superheat in liquids is reviewed in light of the late observations recorded in the literature. The upper superheat limit temperature is shown to be a criterion for flameless vapor explosions.

Reid, R. C., et al., Flameless Vapor Explosions. American Gas Associa Catalog No. M20177, 1977.

Flameless vapor explosions are discussed for a wide variety of substar including LNG. Theoretical explanations are based on the superheat l. temperature.

Reid, R. C. and Smith, K. A, "Behavior of LPG on Water." Hydrocarbon Processing, pp. 117-121, April, 1978.

Russ, R. M., Detection of Atmospheric Methane Using a 2-Wavelength HeNe Laser System. Masters Thesis, Mass. Institute of Tech., June, 1978.

The report describes the design of a system to reliably measure concentrations of methane in air of 0.1 to 100% which may arise in LNG spill tests. Discussions of design requirements, alternatives, and model and laboratory test results are presented.

Santman, L. D., "The Department of Transportation's Role in LNG Safety Regulations." 1978 Operating Section Proceedings, American Gas Association, Montreal, Quebec, May, 1978.

DOT authority over LNG safety is derived from the ports and waterways safety Act of 1972 and the natural gas pipeline safety Act of 1968. Proposed regulatory action on HR.11622 is discussed.

Sidjak, W., Arctic Pilot Project. Presented to the American Gas Associa tion Transmission Conference, Montreal, Quebec, May 8-10, 1978.

This paper describes a pilot study involving a barge-mounted liquefactio and storage facility in the Arctic. The pilot study is in support of the Arctic Islands LNG project (see above).

Simplified Methods for Estimating Vapor Concentration and Dispersion Distances for Continuous LNG Spills into Dikes with Flat or Sloping Floors. A. D. Little, Inc. for American Gas Association, AGA No. X50978, April, 1978.

The report describes a set of techniques which allow calculation of dispersion of LNG spilled on a flat or sloped dike floor. Calculations include leakage flow rate, LNG flash vaporization, LNG boiling and vapor overflow, and vapor dispersion.

Smith, R. V., The Influence of Surface Characteristics on the Boiling of Cryogenic Fluids. J. of Eng. for Industry 91:1217-1221, 1969.

The influence of a solid heating surface on the boiling behavior of liqu helium, hydrogen and nitrogen is being discussed. This is a review arti and contains essentially no new information.

Terry, M. C., "Floating LNG Facilities May Solve Many Problems." Pipeli and Gas Journal, pp. 25-28, June, 1977.

This article discusses the history of development of offshore liquefacti facilities. Various generic types of floating facilities are discussed and their potential evaluated.

Tsai, S. S. and Chan, S. H., A General Formulation and Analytical Soluti for Multi-Dimensional Radiative Transfer in Non-Gray Gases. A.I.Ch.E. A.S.M.E. Heat Transfer Conference, Salt Lake City, Utah, (77-HT-51),

ora, M. K., Shaheen, E. I. and Knieves, G. V., U.S. Energy Future. Are LNG Imports will be Needed. World Oil, June, 1978, pp. 134-148.

he future U.S. energy needs and the potential of LNG imports are discus t is predicted that LNG could supply 4.7% of total U.S. energy require ents by 1985. This would require an import of 4.86 tcf including 1.17 rom Alaska.

Welker, J. R., Wesson, H. R. and Brown, L. E., Use of Foam to Disperse LNG Vapors? Hydrocarb. Process., pp. 119-120, 1974.

ests have shown that a blanket of high-expansion foam effectively redu round-level methane concentrations downwind of an LNG spill.

Wesson, H. R., Lott, J. L., Feldman, R. and Closner, J. J., "Thermal Performance of a Fire Resistant Coating Applied to Prestressed Concrete 1978 Operating Section Proceedings, American Gas Association, Montreal, Quebec, May, 1978.

he fire resistance of coatings designed to protect weakening of pre- tressing wire in cryogenic tanks is tested. Degree of protection with oating thickness is discussed.

Wesson, H. R., Welker, J. R. and Brown, L. E., "Control LNG-Spill Fires Hydrocarb. Process. 51:61-64, December, 1972.

ontrol of LNG-spill fires is obtained by application of high expansion oam. Follow-up with dry chemical fire extinguishers will quickly xtinguish the fire.

Westbrook, C. K., A Generalized ICE Method for Chemically Reactive Flow n Combustion Systems. Lawrence Livermore Lab., UCRL-78915, Rev. 1, ugust, 1977.

he ICE method is modified to allow the pressure calculated at a new ti tep to include the effects of changes in internal energy and species over that time step. This is important for reactive flows in which the hange in temperature and/or species contributes significantly to chang n pressure.

Witte, L. C. and Cox, J. E., Nonchemical Explosive Interaction of LNG a Water. ASME Paper 71-WA/HT-31, 1971.

t is assumed that observed, nonchemical LNG-water explosions can be xplained as vapor explosions. Rapid fragmentation of the LNG is belie o be a necessary precondition for the occurrence of such an explosion.

ang, K., Explosive Interaction of Liquefied National Gas and Organic iquids. Nature 243:221-222, 1973.

mall scale experiments are described in which LNG is poured into organic iquids. In some cases resulting reactions were rather violent, indicating he possibility of vapor explosions.

ubiate, R., Pomonik, G. and Mostarda, S., "Single Point Mooring System or Floating LNG Plant." Ocean Industry, pp. 75-78, November, 1978.

he advantages of portable floating offshore LNG terminals are discussed s a preface to a description of a mooring system for such a facility.

REPORT Q

Liquefied Petroleum Gas (LPG) Safety and Environmental Control Assessment

M. G. Patrick

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
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Operated by Battelle Memorial Institute

TABLE OF CONTENTS

FIGURE

The Department of Energy (DOE) has requested Pacific Northwest La-
tory (PNL) to assess the technological bases for LPG safety and enviro
control provisions and regulations. This is in support of the object
assess the safety and environmental control aspects of processing, st
transporting LPG in the United States. The technological areas being
investigated include vapor generation and dispersion, fires, explosion
release prevention and control. This assessment will include the ide
of any areas where additional work may be needed.

Work on the project was started in July, 1978 at PNL. Elements
work are to be performed by Battelle Columbus Laboratories (BCL), the
of Gas Technology (IGT) and the Applied Technology Corporation (ATC).

INTRODUCTION

Both the Congress and DOE have expressed concerns about the adequ of the safety and environmental control provisions and regulations app cable to LPG. In responding to this concern the DOE has requested PNL assess the technological bases for such provisions and regulations to if any additional work is needed.

As the acronym LPG is used by the industry, it includes propane, and various propane-butane mixtures. LPG is grouped along with natura gasoline, ethane and other materials under the term "Natural Gas Liqu About 75% of these products are obtained from domestic natural gas sou The remainder is represented by "Liquefied Refinery Gases (LRG)," proc from petroleum sources, and foreign imports.

Data from the Gas Processors Association (GPA) indicate that the production of NGL has declined slightly since a peak in 1972, but over been quite stable since about 1974. The GPA also reports that undergr storage of light hydrocarbons (such as LPG) has been increasing at abo per year and reached an estimated capacity of 375 million barrels by t of 1977.

Because about 75% of the LPG comes from natural gas sources, its duction is very closely related to natural gas production. The GPA ex a growing deficit between consumption and domestic production with a r growth in LPG imports. Therefore, the principal growth in LPG is expe in large volume transportation and storage.

PROJECT OBJECTIVES AND SCOPE

Objectives of this project in Fiscal Year (FY) 1979 are to: 1) s the status of current LPG safety and environmental RD&D activities and characterize the present and future LPG industry, covering all operati production to utilization. Port facilities, major storage facilities peakshaving plants, water transport, truck transport, rail transport a pipelines will be described in terms of numbers, locations, process va

ediate size and smaller installations, and containers utilized by wholesa utlets, retailers, industrial users, and domestic consumers will also be ncluded. This work is planned to be sufficiently advanced in FY79 to pro ackground information for a subsequent report which will include an asses ent of the technological bases for safety and environmental control aspec f the LPG industry. It is expected that in FY79 a preliminary version of his report will be reviewed by a group of national experts in industry, overnment and the research/engineering community. The effort planned in ncludes compiling the results of this review and completing the assessmen

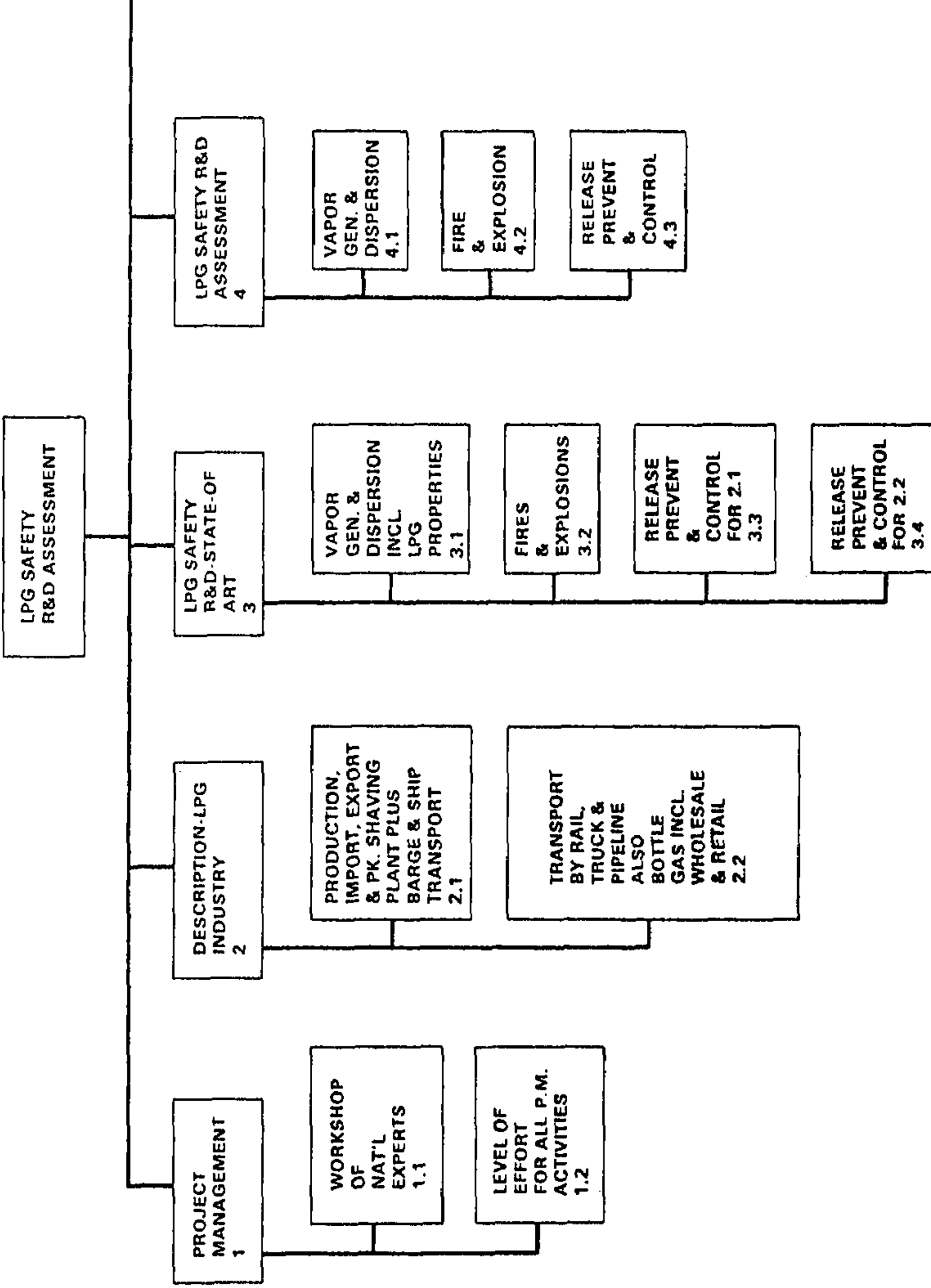
STATUS

A Work Breakdown Structure has been developed for the project. Figur lelineates the project tasks and subtasks. Task 1 is project management. Task 2 has the objective of generating a description of the LPG industry a s considered to be particularly important in this project because the inc ry is over 50 years old and is very widely dispersed geographically. In ddition to identifying the scope of the various segments of the industry he description will also identify the design and fabrication practices, processes used for liquefaction and vaporization, the industry's accident history and growth projections.

Task 3 will identify the status of R&D work which has been done or is in progress in the areas indicated in the subtasks. A draft of the report section describing LPG chemical, thermal and physical properties has been completed by BCL and is currently under review. Work on the other subtas in Task 3 is progressing.

Results from Tasks 2 and 3 will be compiled into a preliminary report Task 5 and issued to a group of national experts in advance of the worksh indicated as subtask 1.1.

In FY80, Task 4 is expected to be activated. This is intended to as the adequacy of safety and environmental R&D accomplished. Major inputs


LPG SAFETY R&D ASSESSMENT
PROJECT MANAGEMENT 1
WORKSHOP OF NAT'L EXPERTS 1.1
LEVEL OF EFFORT FOR ALL P.M. ACTIVITIES 1.2
DESCRIPTION-LPG INDUSTRY 2
PRODUCTION, IMPORT, EXPORT & PK. SHAVING PLANT PLUS BARGE & SHIP TRANSPORT 2.1
TRANSPORT BY RAIL, TRUCK & PIPELINE ALSO BOTTLE GAS INCL. WHOLESALE & RETAIL 2.2
LPG SAFETY R&D-STATE-OF ART 3
VAPOR GEN. & DISPERSION INCL. LPG PROPERTIES 3.1
FIRES & EXPLOSIONS 3.2
RELEASE PREVENT & CONTROL FOR 2.1 3.3
RELEASE PREVENT & CONTROL FOR 2.2 3.4
LPG SAFETY R&D ASSESSMENT 4
VAPOR GEN. & DISPERSION 4.1
FIRE & EXPLOSION 4.2
RELEASE PREVENT & CONTROL 4.3

from the workshop of national experts. This assessment will provide t
for defining additional work that may be needed.

In summary, work is progressing in the following areas:

- A literature search
- A description of the various segments of the LPG industry
- A compilation of the chemical and physical properties of LPG
- A status review of RD&D relating to predicting consequences of LPG fires
- A status review of RD&D in the areas of vapor generation and dispersion from LPG spills.

Contact has been established with the Gas Processors Association the National Liquefied Petroleum Gas Association (NLPGA), the Applied Technology Corporation (ATC), and Dr. Robert Reid at MIT, to obtain in mation.

LPG Safety Research

J. R. Welker

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract EP-78-C-05-6020

Applied Technology Corporation
Norman, Oklahoma 73070

FIGURE

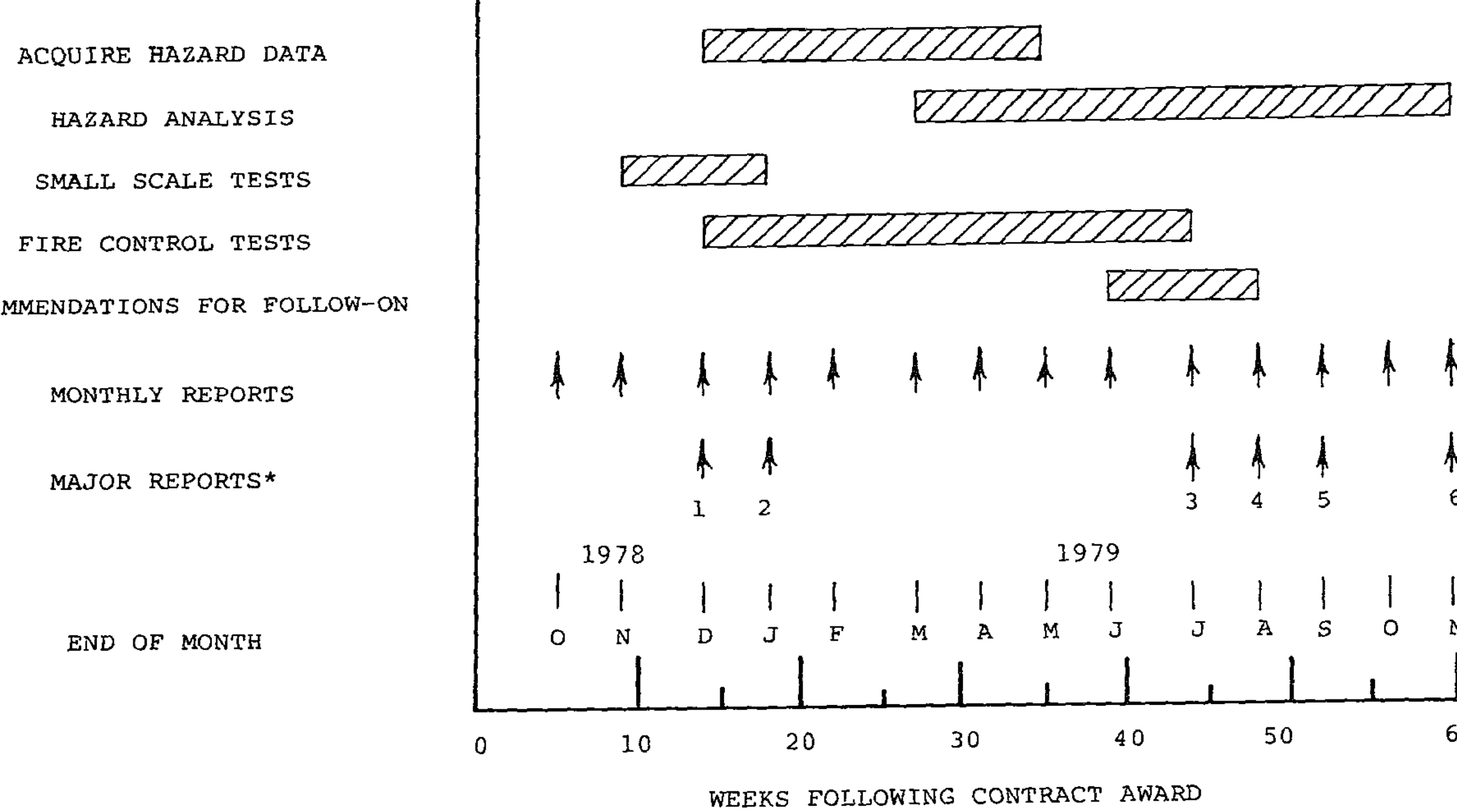
The goal of Contract EP-78-C-05-6020 is to analyze the hazards of mar sportation of LPG and determine fire-fighting agent effectiveness for control using dry chemicals and high expansion foam. As part of the rd analysis, an annotated bibliography will be prepared. A preliminar on of this bibliography is included as Report T in this Status Report

This project has just started, and no data from the field experiments he hazard analysis are available.

Work performed under Contract No. EP-78-C-05-6020 was initiated n
end of September, 1978. Because of the very short time during which t
project has been underway, this report will present only a brief discu
of the work accomplished to date. A summary of the work planned for t
ensuing year with approximate milestones for portions of the project w
also be provided.

The work is programmed to follow the schedule shown in Figure 1.
re two minor (in terms of effort) tasks and four major tasks to be co
Two of these tasks are already well underway and initial work has been
started on a third.

Task 1 is the preparation of an annotated bibliography related to
n LPG production, transportation, and utilization. This portion of t
work is currently well underway. It is programmed to continue through
most of the period covered by the project, but the major portion of ob
materials for the bibliography will be completed during the first six
eight months. The program schedule shows the initial bibliography is
prepared and submitted at the end of December, 1978. This work has be
speeded up as much as possible, and appears in this report as Report T
s obviously not exhaustive because of its preliminary nature. A more
plete bibliography with notes and comments is scheduled for completion
near the end of September, 1979. The bibliography includes references
LPG and other materials in instances where experience with other mater



*MAJOR REPORTS: 1-Initial Bibliography, 2-Small Scale Tests, 3-Fire Control Tests, 4-Follow-on Recommendations, 5-Draft Final Bibliography, 6-Draft Final Report.

r the end of December will be informal, and will be an enlargement of port T including the latest publications received.

Task 2 will acquire data for LPG hazard analyses. The initial work ncentrate on marine transportation of LPG. A number of requests for formation on LPG tanker design, LPG barge design, and LPG shipping and ansfer operations have been sent to various companies engaged in LPG mmerce. Only a few replies have been received so far, but others, who ve not replied, have promised substantial help in the form of diagrams ip and terminal design and information on operational procedures. Thi sk was started early in order to provide a longer time to acquire info tion related to current practices in LPG marine trade and avoid delays the hazard analysis task.

Task 3 is a hazard analysis for LPG marine operations. It is sched begin in early 1979 following several months of effort to acquire the ta required to construct a composite model of the operations as curren acticed.

Task 4 is one of the smaller tasks designed to provide preliminary formation for a later task. Small-scale spills of LPG will be made to eck out some of the boiling rate and burning rate sensors that will be ed on larger scale tests. The response of liquid level sensors will b mpared with the results of direct weight loss measurements to assure t rning rate measurements can be made during large scale fire tests. Ta

is well underway, and preliminary tests will be run before the middle o December, 1978. The field work will be completed and a report of the r submitted about the end of January, 1979. Since the major purpose of t tests is to check equipment for large scale tests, it is not expected t significant new data on LPG behavior will be developed.

Task 5 will provide data on fire extinguishment and control for LPG fires. The fire tests will be run in concrete pits ranging from 5 ft sq to 40 ft square. Previous tests (using LNG) have shown that the size ra provided by these tests will be sufficient to allow use of the results fo fire sizes of practical interest in LPG production, utilization, and tran portation. The fire extinguishment studies will utilize sodium bicarbona potassium bicarbonate, and urea-potassium bicarbonate dry chemicals. Eac the agents will be applied over a range of rates and the effect of powder application rate on extinguishment time will be determined. The goal is find the best application rate for controlling LPG fires. High expansion foam will be investigated to find how fast it must be applied to control L ires and how effective the control will be in terms of the reduction of adiant fluxes from the fire. As part of the fire control and extinguishm ests, a small amount of data on LPG burning rates, boiloff rates, radiati luxes, and flame behavior will be taken. This additional information wil e useful as inputs to modeling studies on LPG fires. The fire control te re scheduled to begin as soon as weather and site availability permit, mos kely in early 1979. The actual testing period will be as brief as possib reduce costs associated with supplying refrigerated LPG to the test site

spersion, fire radiation, and flame modeling as well as pointing the
hazard analyses in the areas of production, rail transportation, and h
transportation of LPG.

REPORT 5

Simultaneous Boiling and Spreading of Liquefied Petroleum Gas (LPG) on Water

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Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
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TABLE OF CONTENTS

FIGURES

spilled on water have been reviewed. All were found to have questior assumptions and require experimental data to indicate the plausibilit the assumptions.

The models did, however, provide an approximate base upon which plan experimental tests. A one-dimensional water-filled channel is r being constructed to allow measurements of the rate of spread and eva ation for LPG spilled in one end. Vapor concentrations, vapor and li temperatures, and high-speed movies will be used to quantify the resu

troduction

Liquefied petroleum gas (LPG) is often transported in bulk within
rge insulated tankers. An accidental spill of such fluid on water,
ere spreading and evaporation would occur simultaneously, may lead t
serious hazard since LPG boils well below ambient water temperature
rms a combustible (and, possibly, an explosive) cloud which is non-
oyant and not readily dispersed. In order to assess the potential h
used by the liberation and subsequent dispersion of vapor, it is ess
know the simultaneous boiling and spreading rates of LPG on water,
ze and the shape of spill, and the time scales over which the vapor
released.

In the present work, it is planned to measure experimentally and
eoretically the simultaneous boiling and spreading rates of LPG upon
ter surface.

evious Work

A literature review has shown that few experiments have been made
termine the spreading and boiling rates of any volatile cryogen on w
st previous studies have been of a theoretical nature and were based
edominantly upon results from nonvolatile oil spreading.

The mechanics of cryogen spreading on water parallels to a large
tent the spread of oil slicks over water. The major distinction bet
e two processes is the associated mass loss by evaporation of cryoge
om an order-of-magnitude estimation, Fay (1969) deduced three princi
gimes of flow which exist for the spread of an oil spill on water.
rly times, the spreading is caused by a hydrostatic pressure differe
tween the oil and water. The rate of spread is retarded primarily b

a balance of the gravity force and the retarding viscous force a water interface. At very late times, further spread is forced b tension and opposed by viscous forces. Relative to the spread o evaporation of all the liquid is expected to be completed before regime would be established.

Burgess et al. at the Bureau of Mines (1970) studied LNG sp open pond and reported that LNG spead at a constant velocity of Experimental data taken by Burgess et al. showed pool diameters function of time for spills of LNG up to 0.5 m^3. In general the

$$d = 0.76\ t\ (\dot{m})$$

was obeyed in the early part of the test but the spreading rate with time.

Boyle and Kneebone (1973) made spills of LNG on a pond and the pool diameter when it began to break up into discrete patche claimed that, when the thickness of LNG reached approximately 1. there was no longer a coherent layer and discrete patches of LN neously formed. Also, they claimed that in a spreading situati not form and boiling rates would be expected to be quite low co confined area spills where ice developed and most boiling occur nucleate region on a thin ice crust.

For LPG spills, it is believed that the very rapid ice for will occur simultaneously with spreading and thus the confined results would be applicable.

Previous analyses have concentrated on the case of the so- instantaneous spill in which the time required for all the liqu

after contact with water.

With the further assumption that there is an applicable "mean film thickness" to characterize the cryogen layer at any time, Raj and Kalel (1973) proposed a radial spreading model of cryogen over a water surface that included the effects of evaporation. An expression for the rate of spread was obtained by equating the gravitational force, F_g, to the inertial resistance force, F_i, where

$$F_g = \pi r h^2 \rho_L g \Delta \quad (2)$$

$$F_i = -C(\pi r^2 h \rho_L)(d^2r/dt^2) \quad (3)$$

h is the thickness of the spill and Δ is defined as $[(\rho_{H_2O} - \rho_{cryogen})/\rho_{H_2O}]$. According to the authors, the factor C is introduced to take into account the fact that the inertia of the entire system is a fraction, C, of the inertia of the total mass, assuming that entire mass were accelerated at the leading edge acceleration d^2r/dt^2. They assume that this fraction remains the same at all times. Equating (2) and (3) they obtain the spread law:

$$h = -C(r/g\Delta)(d^2r/dt^2) \quad (4)$$

At the same time, they consider the vaporization of the cryogen with the following mass conservation equation.

$$\rho_L V(t) = \rho_L V_o - \pi \int_0^t \frac{\dot{q} r^2}{\Delta H_{vap}} \, dt \quad (5)$$

where V_o is the original volume spilled and ΔH_{vap} is the latent heat of

a third order nonlinear differential equation. Therefore, four bounda conditions are required to specify the solution, including the unknown of C. The only boundary condition specified explicitly by Raj and Kal is that $V = V_o$ at $t = 0$. The remaining three constants are obtained b making their solution (for the case of a non-evaporating fluid) identi to that of Fannelop and Waldman (1972). For the case of constant $\dot{q}$, R Kalelkar obtain the following expressions for the time at which all th liquid evaporates and the maximum pool radius

$$t_e = 0.6743 \left[\frac{V_o \rho_L^2 \Delta H_{vap}^2}{g \Delta \dot{q}^2}\right]^{1/4}$$

$$r_{V_{max}} = 1.0059 \left[\frac{V_o^3 \; \rho_L^2 \Delta H_{vap}^2 \; g\Delta}{\dot{q}^2}\right]^{1/8}$$

According to the above equation, the time to complete vaporization va with the fourth root of the volume spilled.

Otterman (1975) has reviewed various models for spreading cryoge on water. Essentially, all the models are based upon derivations whic consider (in the early time period after a spill) that the gravity fo cause spreading while being opposed by inertial forces. In such case without evaporation,

$$r = k(g\Delta V_o)^{1/4} \; t^{1/2}$$

where k is a dimensionless constant which, from experiment and theory 0.841. Then the radial spreading velocity is given by

Eq. (8) shows that the radial spreading velocity is proportiona $t^{-1/2}$; i.e., the spreading rate decreases with time, a fact observed not used by Burgess et al. (1970). Using Eq. (8) in a model which a a constant heat flux, the analog to Eq. (6) is

$$t_e = 0.949 \left[\frac{\rho_L^2 \Delta H_{vap}^2 \; V_o}{g\Delta \dot{q}^2}\right]^{1/4}$$

Compared to Eq. (6), Eq. (10) predicts a higher value of t_e.

Raj (1977) developed an expression for one-dimensional spreadi based on the same assumptions as Raj and Kalelkar (1973). With x e to the spread distance and w the constant duct width, equating the tational force to the inertial force, a pseudo-equilibrium relation was obtained.

$$F_{gr} = (wh^2)(\rho_L g\Delta)/2$$

$$F_{in} = -k_{1D}(wxh)(\rho_L)(d^2x/dt^2)$$

Equating,

$$h = -2k_{1D}(x/g\Delta)(d^2x/dt^2)$$

together with mass conservation equation

$$V = V_o - (w/\rho_L \Delta H_{vap}) \int_0^t \int_0^x \dot{q} \; dx \; dt$$

and

$$V = wxh$$

constant boiling heat flux, he obtained the following equat
spread distance and the time to complete vaporization.

$$x_{max} = 1.59 \left[\frac{(V_o/w)^3(g\Delta)}{(\dot{q}/\rho_L \Delta H_{vap})^2}\right]^{1/5}$$

$$t_e = 1.09 \left[\frac{(V_o/w)^2}{(g\Delta)(\dot{q}/\rho_L \Delta H_{vap})^3}\right]^{1/5}$$

According to Eq. (17), the time to complete vaporization va
two-fifths of the spill volume.

Recently, Georgakis et al. (1978) proposed a model for
spills of liquid fuel on water resulting from collision and
fuel tank aboard ship.

As mentioned above, in the prior analyses of instantan
the shape of the spill was taken to be circular. The spill
depends only on the spill volume, neither on geometrical ch
of the ruptured tank nor on the hole size and location in t

Georgakis and his co-workers took account of these eff
presented a model to predict the time variation of the shap
sions of liquid fuel spills on water. In contrast to the c
of an instantaneous spill, the predicted shapes of the hole
found to be long and narrow. The maximum spill area is fou
significantly less than that for an instantaneous spill of
as is the time to attain the maximum area.

However, the authors, in their derivations, assume that hydro equilibrium is established in the vertical direction as the fuel l the tank and that the displaced water travels with the same veloci the fuel. This leads to a situation where conservation of mass is achieved. Furthermore, on physical grounds, the velocity of the f interface could be the same as the fuel velocity, but the velocity displaced water is not expected to be the same as the fuel.

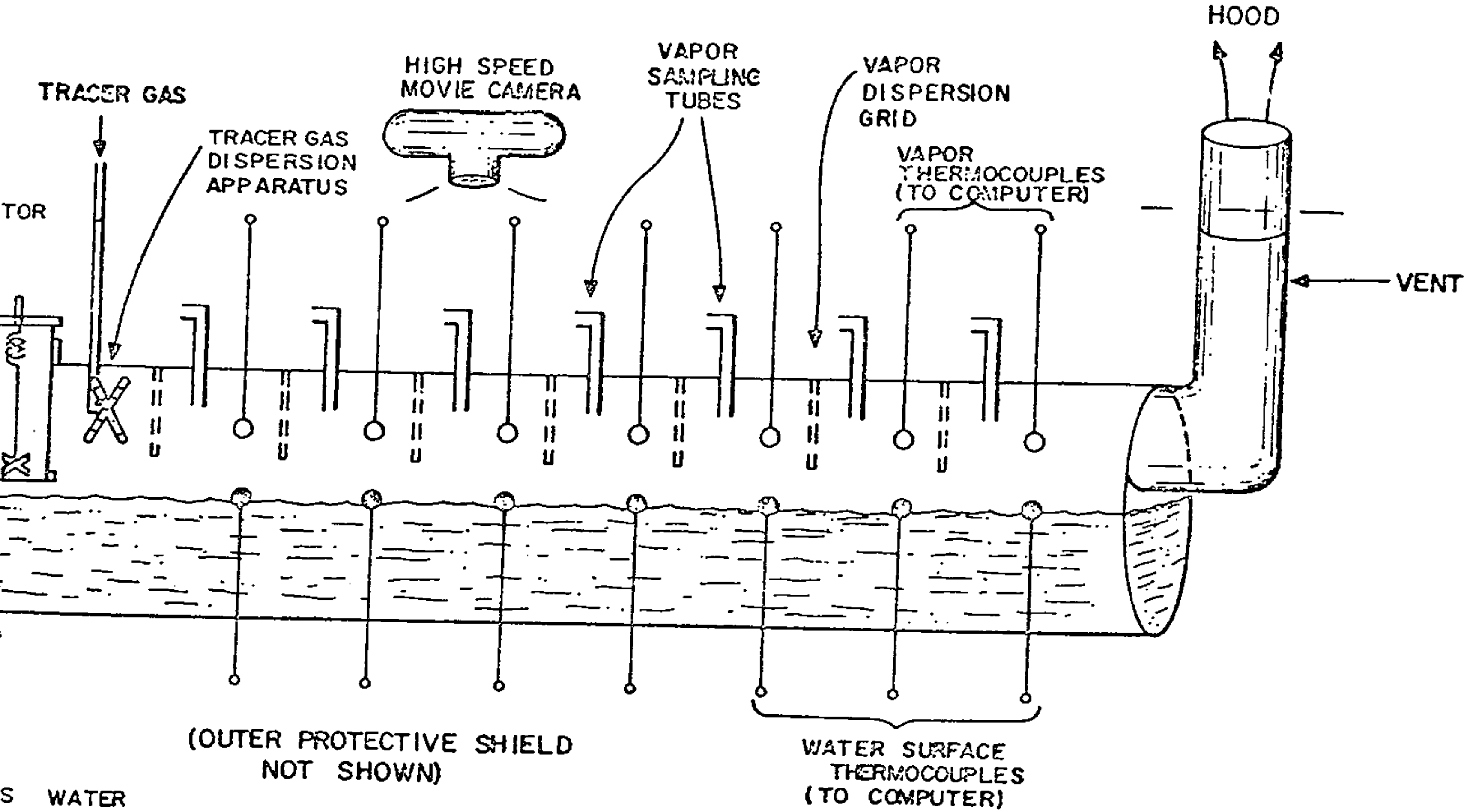
In spite of the assumptions and limitations of this paper, it provide a somewhat more realistic basis for an actual spill.

Apparatus

Simultaneous boiling and spreading tests are to be carried ou long, narrow water trough. The trough will be covered to duct the hydrocarbon gases into a hood. All sections are to be fabricated transparent material to allow visual observation.

A schematic representation of the test apparatus is shown in This apparatus allows only one-dimensional rather than radial stud Water is to be held in the horizontal tube and LPG or a simulant is spilled on the water at one end. In order to study the charact of this process, one must be able to measure, or otherwise determi mass evaporated, the composition of the liquid and vapor, and the temperatures, as functions of time and position.

Since the water trough cannot be positioned on a load cell, local boil-off rates of LPG on water are to be monitored in an in manner. An inert tracer gas (i.e., He) will be introduced contin at steady state at the end where the LPG is spilled. The concent of the tracer gas are to be measured with sampling devices during

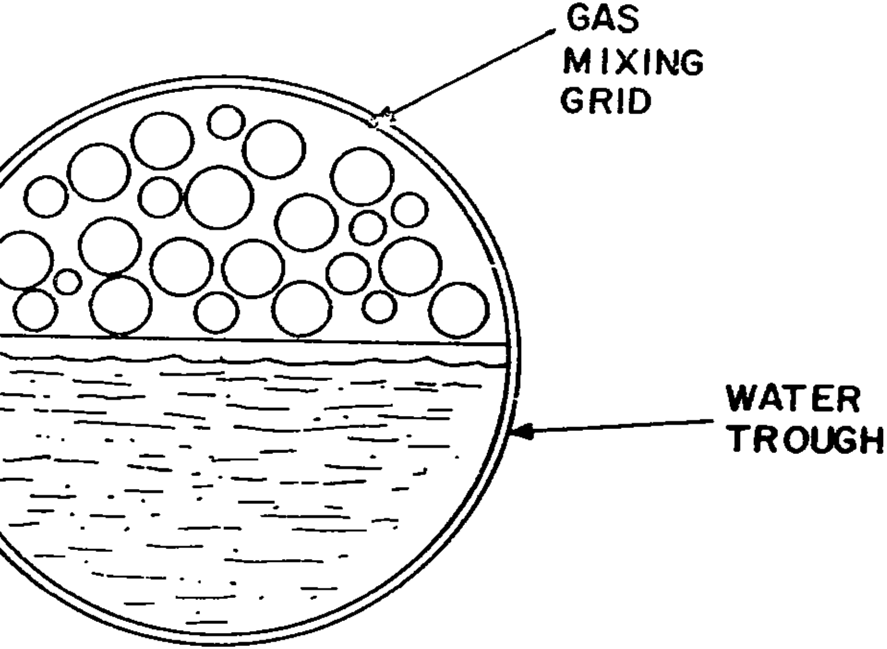

HOOD
VENT
TRACER GAS
TRACER GAS DISPERSION APPARATUS
HIGH SPEED MOVIE CAMERA
VAPOR SAMPLING TUBES
VAPOR DISPERSION GRID
VAPOR THERMOCOUPLES (TO COMPUTER)
TOR
(OUTER PROTECTIVE SHIELD NOT SHOWN)
WATER SURFACE THERMOCOUPLES (TO COMPUTER)
S
WATER

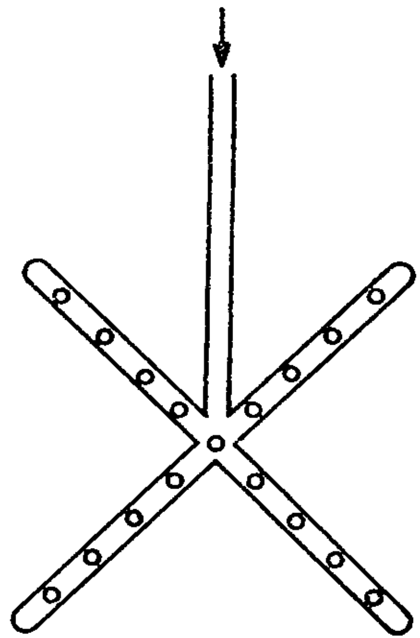
experiment at different sections downstream from the spill. Then the ma boiled off as functions of time and position can be obtained.

Eight sampling stations are proposed (seven are shown in the sketch an eighth would be in the hood vent). Each of these stations have the capacity to collect six separate samples over the duration of an experim run (about 30 seconds). Each sampling station, therefore, consists of evacuated sample bottles and solenoid valves. A 5-TI programmable-contr system is to be used to provide a signal to open and close the solenoid valves at definite preprogrammed times. (The sampling time will be betw 1-2 seconds.) Furthermore, water, cryogen, and vapor temperatures are t be measured by thermocouples whose output will be fed into a NOVA-840 real time computer.

The water trough, elevated by wooden supports, will consist of Ple tubing 17.8 cm O.D., 16.5 cm I.D., and 4 m long. There will be several grids, shown in Figure 2-a, along the top of the duct for the purpose o enhancing the mixing of the LPG vapor and the tracer gas. Also, several alternative designs for the mixing of gases will be tested. The tracer gas will be injected using a dispersing apparatus illustrated in Figure

Simply spilling the cryogen from the opening of the trough would cause a severe disruption on the water surface and the inertial impacti forces would set up waves within the tube with possible wave reflection from the far end. In order to reduce these effects, a cryogen distribu shown in Figure 3, will be used. It is being constructed from a 0.64 c thick acrylic tube; the inside cross-sectional area is 154 cm^2 and the length is 20 cm. An elastic-rubber membrane is stretched and placed to cover the bottom end of the tubing and held in place with an adjustable





CROSS SECTION VIEW)

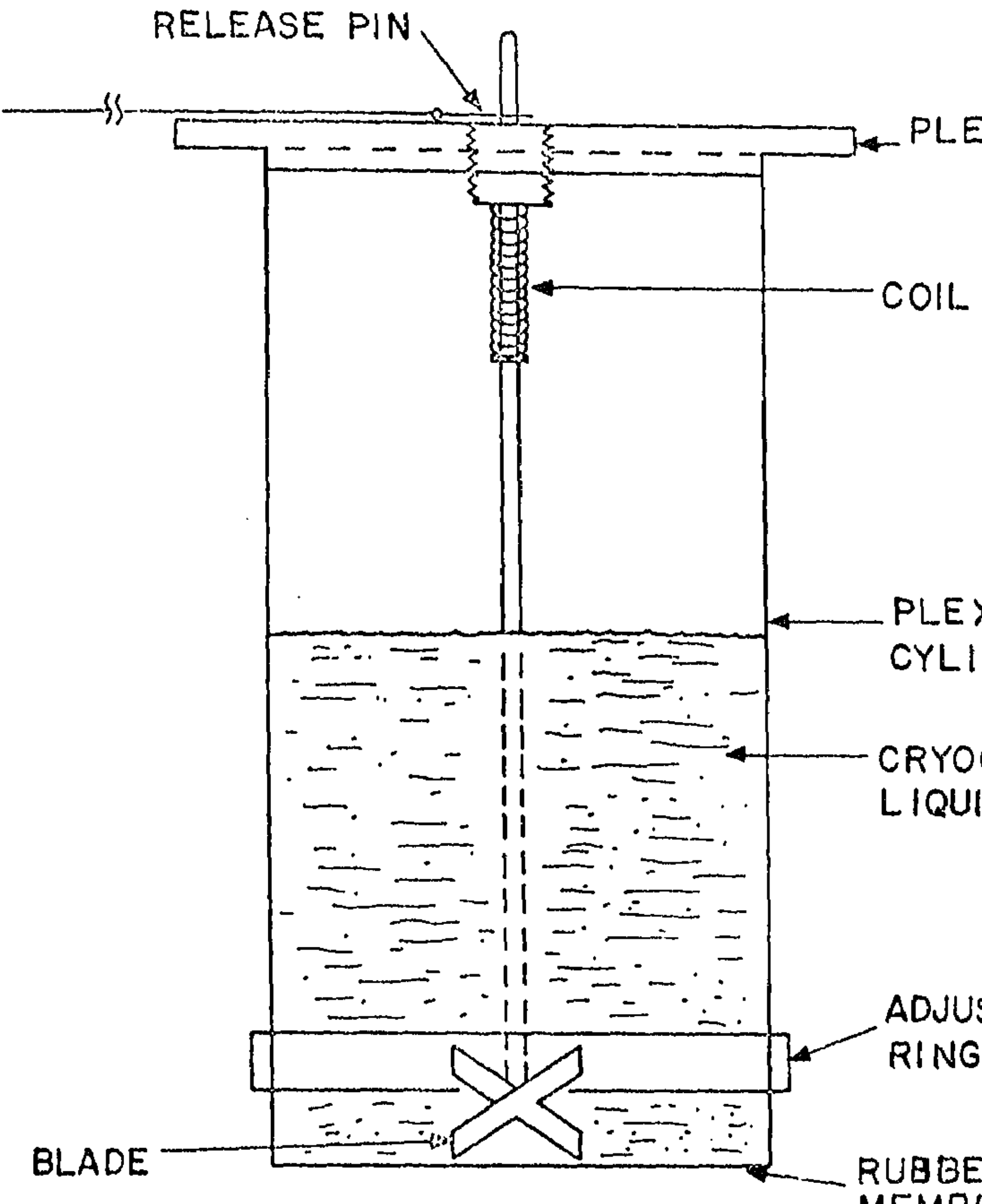


Figure 3 LPG Liquid Distributor

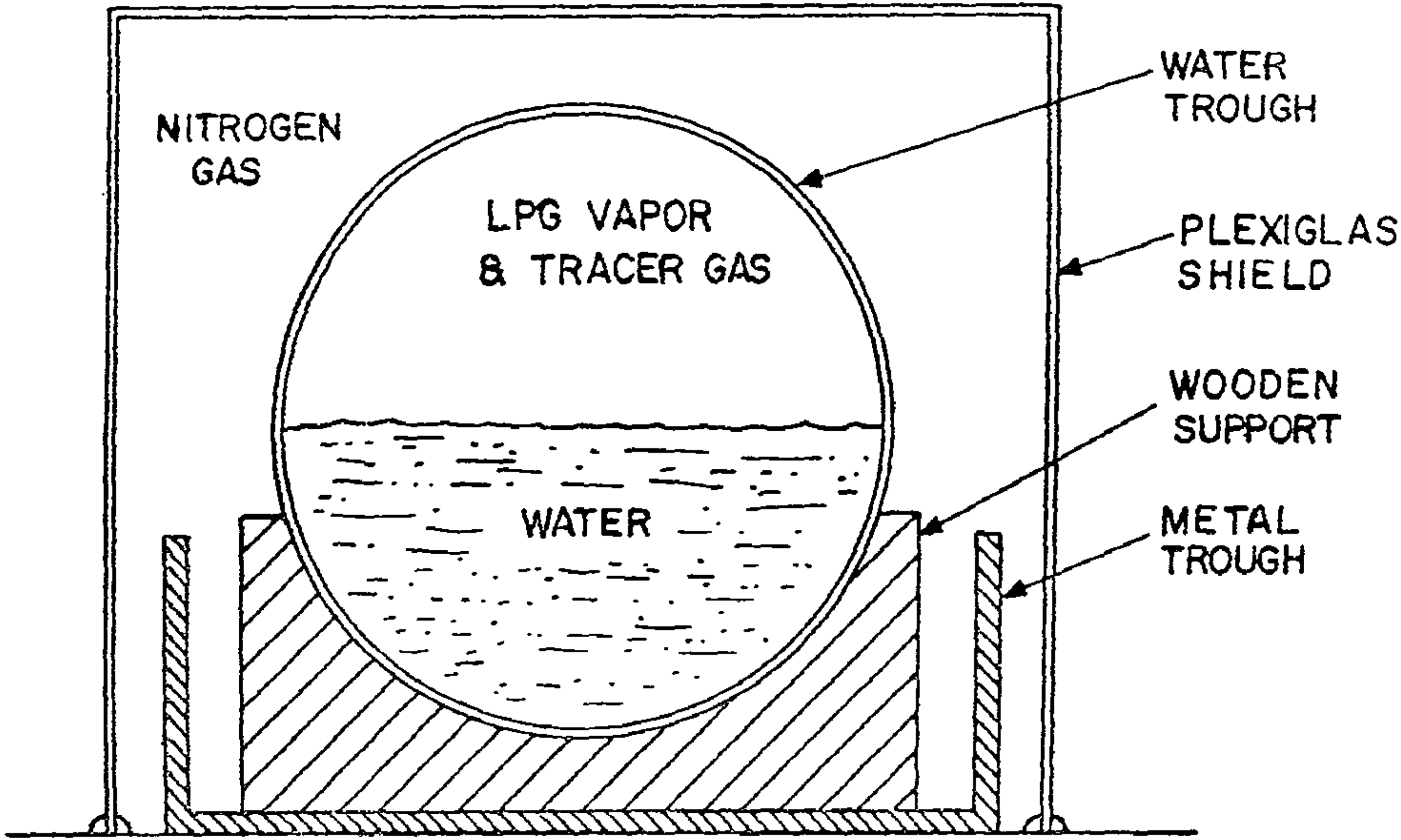
a fraction of a second. This allows the cryogen to fall in a plug-like fashion and contact the water.

Water, cryogen, and vapor temperatures are to be monitored by a set chromel-constantan thermocouples. All thermocouples are heat-stationed, i.e., a section of bare thermocouple ware will be exposed to the same temperature to minimize axial heat conduction. Seven vapor thermocouples fabricated from 25 μm wire, enter through the top cover of the water trou Also, seven liquid thermocouples, fabricated from 127 μm wire, are to be introduced through the bottom and placed at the water surface to indicate the passage of LPG; thus the rate of spread can be measured. Furthermore a high speed camera will be used to record the movement of the LPG, the ice growth, and bubble formation.

For safety purposes, the water trough, including the wooden supports will be placed within a metal U-shape container. In the event of breakag all of the fluid would be retained. Furthermore, in order to prevent ambient air from mixing with the light hydrocarbon gases in the event of breakage, a rectangular Plexiglas frame will completely enclose the exper mental apparatus. Nitrogen is then introduced into the outer Plexiglas frame to purge the surrounding space of air. An end view of the safety trough and Plexiglas shield set-up is shown in Figure 4.

Results to Date

As mentioned in the Renewal Proposal for 1978-1979, the principal experimental difficulties lie in sampling the gas at different locations- at known times--during the very brief experiments. Another problem is th



(CROSS SECTION VIEW)

completed at the end of January, 1979.

Boyle, G.J. and A. Kneebone, "Laboratory Investigations into t
istics of LNG Spills on Water Evaporation, Spreading, and Vap
Shell Research Ltd., Thornton Research Centre, Chester, Engla

Burgess, D.S., J.N. Murphy, and M.G. Zabetakis, "Hazards of L
Marine Transportation," U.S. Bureau of Mines, February 1970.

Fannelop, T.K. and G.D. Waldman, "Dynamics of Oil Slicks," A.
(4), 506-510 (1972).

Fay, J.A., "The Spread of Oil on a Calm Sea," Oil on the Sea,
D.P. Hoult, Plenum Press, New York, 1969.

Georgakis, C., J. Congalidis, and G.C. Williams, "A Model for
Instantaneous LNG and Gasoline Spills," submitted to Fuel, 19

Otterman, B., "Analysis of Large LNG Spills on Water. Part 1
Spread and Evaporation," Cryogenics, 455-460, August 1975.

Raj, P., Personal communication, 1977.

Raj, P. and A. Kalelkar, "Fire Hazard Presented by a Spreadin
Pool of LNG on Water," presented at Combustion Institute (USA
Section Meeting (1973).

Preliminary Annotated Bibliography of Publications Related to Fire Safety in Marine Import of Liquefied Petroleum Gas

J. N. Ice
N. M. Butcher

Prepared for the
Division of Environmental Control Technology
U.S. Department of Energy
under Contract EP-78-C-05-6020

Applied Technology Corporation
Norman, Oklahoma 73070

REPORT T

TABLE OF CONTENTS

This preliminary bibliography is part of a longer-term literature su
fort being conducted for the U.S. Department of Energy. This survey is
btask designed to generate specific and generic information relating to
e safety of Liquefied Petroleum Gas in the marine environment. This i
tion includes equipment failure rates and frequencies, specific and gen
uipment failure mode and effects analyses, and the development of fault
ee analyses for the analysis of spill and fire hazards. This prelimina
sting is not a scheduled report under the contract and is only a portio
e contents expected to be included in the final bibliography. Conseque
e major effort has been to identify and begin acquisition of published
ich are expected to provide usable data for the main task of hazard ana

Because this subtask relates to the hazard analysis task specificall
e final bibliography may not provide complete coverage of all spill and
formation. No documents are listed which have not been reviewed by the
me of the categories of information contained in this bibliography incl
e following:

1. Failure data for LPG-related or LPG analogous equipment

2. Casualty and/or accident frequencies for LPG production, transport, and use

3. Current risk reduction efforts in the LPG industry
4. Failure mode and effects data for LPG-related equi
   and processes
5. Procedures, regulations, codes, and standards
6. Marine vessel and terminal facility designs and op
7. Process flow loops, capacities, rates
8. Physical properties data
9. Quantitative fire extinguishment and control data
10. Present fire control procedures
11. Evaporation rate and dispersion data
12. Explosion potential data
13. Burning rates and flame size data
14. Heat transfer data, radiation and convection

The final report on this contract, including the annot
bibliography, is due in December, 1979.

American Petroleum Institute, "Liquefied Petroleum Gas Report," January - (1978).

A monthly listing of all U.S. LPG inventories for the first 10 months of 1978 is presented. Graphs are included for total inventor of propane, butane, etc., to allow comparison with 1976 and 1977 inventories.

Authen, T. K., and E. Skramstad, "Gas Carriers--The Effects of Fire on the Cargo Containment System," Gastech 76, LNG/LPG Technol. Congr. Proc., New York (October 5-8, 1976).

Two different cargo containment systems for LNG are considered for which there are two major analyses presented: 1) A thermal analysis of the heat transfer and temperature distribution in a hull exposed to fire, and 2) analysis of the effect of high temperatures on the cargo containment system and the hull.

Balthasar, H., "The Linde Multi-Vessel-Tank (MVT) for Marine Transportation of Liquefied Gases," Marine Engineers Review, 44, (46 44-46, (July 1975).

A new design for a liquefied gas transport ship is presented. This design uses a large number of relatively small volume aluminum pressure cylinders for storing the liquefied gas during transport. Advantages of the new design are said to include ease and speed of construction.

Bonekemper, Edward H., III, "LNG/LPG Marine Terminal Safety," 56th, Proceedings Annual Convention Gas Processors Association, Technical Paper, Dallas, Texas (March 21-23, 1977). Published by Gas Processors Association, pp. 106-110, Tulsa, OK (1977).

Presentation centers on safety and environmental hazards of LNG and LPG (emphasis is mostly on LNG). United States Coast Guard regulations for liquefied gas ship design, construction, inspection, and operation, as well as proposed regulation on Liquefied Natural Gas Transportation Act discussed. General procedures for USCG inspection of liquefied gas vessels reviewed.

Boudet, Rene, "Shipping and Terminals," 56th, Proceedings Annual Convention Gas Processors Association, Technical Paper, Dalla TX (March 21-23, 1977). Published by Gas Processors Association, pp. 137-138, Tulsa, OK (1977).

(Continued).

The world wide fleet of LPG/NH_3 carriers is reviewed. Estimates are made as to the fleet makeup until 1980. The supply/demand of LPG/NH tankers until 1982 is predicted. U.S. LPG import terminals are reviewed (both terminals in operation and under study). The economics of LPG transport by large (70,000 CBM) tankers are presented. The conclusions reached are: 1) most new LPG/NH_3 tanker capacity will be in the 50 - 75,000 m^3 range, 2) over tonnage in the LPG/NH_3 shipping trade will exist until 1979-82, 3) major additions to U.S. LPG import terminal capacity are needed, and 4) the present market rate for LPG transportation to the U.S. from the Persian Gulf is far below the rate computed for large capacity vessels.

Boyd, R., "Marine Transportation of Refrigerated LPG and Ammonia," Part I, Marine Engineers Review, 37, (42), 37-42, (May 1971).

The design and operation of a typical LPG tank ship is presented in some detail. Topics discussed include cargo tank design, insulation inert spaces, inert gas generators, reliquefaction units, cargo piping, and instrumentation. Safety aspects of these topics are considered.

Boyd, R., "Marine Transportation of Refrigerated LPG and Ammonia, Part II, Marine Engineers Review, 37, (39), 37-39, (June 1971).

The design and operation of a typical LPG tank ship is presented in some detail. Topics discussed include installation of the cargo handling system, operation of the cargo handling system during loading and unloading, and particular problems associated with LPG cargoes. Safety aspects of these topics are considered.

Calvert, D. W., "Historical Market Demand," 56th, Proceedings Annual Convention Gas Processors Association, Technical Paper, Dallas, TX (March 21-23, 1977). Published by Gas Processors Associatio pp. 139-140, Tulsa, OK (1977).

A brief sketch of the market demand for LP-gas in 1976. At that time, 13 percent (1 billion gallons) of the domestic supply of propane was met by imports and imports were projected to be 20 percent of the U. S. market (3 billion gallons) in 1978. Approximately 40 percent of the imported LP-gas is butanes which do not have an established market demand. New markets are expected.

Carpenter, M. H., and L. P. Aarrestad, "The Design of a Simulat
Offering Training in LNG/LPG Cargo Handling," Gastech 76, LNG/LPG Conference, New York (October 5-8, 1976).

Qualitative discussion of ship simulator for crew training. No useful technical information.

Caudle, D. D., and J. D. Alexander, "Propane Adsorption Data fo
Gas Plant Design," 48th Annual NGPA Convention, pp. 105-108, (1969).

Discusses experimental development of dynamic adsorption capaci
for propane. Not directly pertinent in hazard analysis.

Chakraborty, Sunil K., Bholanath N. Mukhopadhyay, and Bimal C. Chanda, "Effect of Inhibitors on Flammability Range of Flames Produce
from LPG/Air Mixtures," Fuel, 54 (1), p. 10-16, (January 1975).

A study of inhibition of flammability limits and burning velocities for flames from an LPG/air mixture, using chlorinated hydrocarbons as inhibitors. Inhibitors used were methylene dichlorid
chloroform, and carbon tetrachloride, listed in ascending order of inhibition efficiency. An increasing number of dissociable chlorine atoms reduced maximum burning velocity (which is associated with propagation to detonation) and narrowed flammability limits, increasi
the lower limit and decreasing the upper limit. This study is useful
background for theoretical examination of mode of operation of fire extinguishing agents.

Colburn, L. E., D. McAdams, and J. F. Smolinski, "LP-Gas Termir
Design Reduces Holding Horsepower Requirements," Oil Gas Journal, 75,
(35), p. 47-51 (August 30, 1976).

Discussion of a refrigeration scheme developed by Adtek, Inc. for handling higher percentages of ethane in the propane product. This scheme significantly reduces horsepower requirements during the holding period before sendout. Application of the refrigeration scheme discussed in relation to the Greater Winnepeg Gas Company's peakshaving facilities, process design of the refrigerated propane, storage facility, refrigeration load, refrigeration system, and mechanical design, especially in relation to safety.

Cook, W. B., W. M. Prindible, and Ing. Bambang Sumatri, "Design Requirements for a Major Offshore Processing Facility," Offshore Technological Conference 8th Annual Proceedings, Houston, T)
(May 3-6, 1976). Volume I, Paper OTC 2483, p. 633-642.

Discusses design details of a sea based LPG processing facilit

Coulter, John L., "Refrigerated LPG Storage and Loading Facilitie in Kuwait," 43rd Annual NGPA Convention, pp. 40-43, (1964).

Describes propane and butane storage facilities of the Kuwait Oil Company. Propane is stored at -45°F and butane at +20°F. 100,000 and 120,000 barrel double walled cylindrical tanks are used for propane storage, while butane is stored in two 65,000 barrel single walled spherical tanks. Information is given as to refrigeration equipment, relief valving and pump motor size. Mention is made of an LPG tank failure due to overpressure resulting from an accidental blockage of the propane flare (vent) line by liquid butane (no other details are given).

Culberson, S. Frank, "LPG/Energy-Value Relationships," 56th, Proceedings Annual Convention Gas Processors Association, Technical Paper, Dallas, Texas, (March 21-23, 1977). Published by Gas Processors Association, Tulsa, OK, pp. 147-151, (1977).

Discusses methods of forecasting LPG import. No safety informati

de Talhouet, M. Loic, "Sea Transport of LPG and Ammonia," Tanker and Bulk Carrier, 18, (12), 10-14 (April 1972).

The world traffic in LPG/NH_3 is discussed. A discussion of transportation techniques, including the steps necessary when changing cargoes, is presented. The conclusion is that there are present econom difficulties in the liquefied gas trade due to an over supply of ships. This problem will continue until the 1980's.

Dick, M. N., and M. H. Tims, "The Prediction of Vapour Offtake Rates from LPG Cylinders," Journal of the Institute of Fuel, 43, (357), 407-412 (October 1970).

A mathematical model for predicting vapor offtake rates from LPG cylinders is presented. Results from experiments on small LPG cylinder show good agreement with the model. The model predicts the composition of the vapor being withdrawn and the remaining liquid, the liquid tempe ture, and cylinder pressure at any time.

Drake, Elisabeth M., Ayodeji A. Jeje, and Robert C. Reid, "Transi Boiling of Liquefied Cryogens on a Water Surface," Part I. Nitrogen, Methane, and Ethane, Int. J. Heat Mass Transfer, 18, 1361-1368 (1974).

(Continued).

Reviews previous related work and presents results from experime studies of transient boiling rates of pure liquefied nitrogen, methane and ethane on a water surface. These experiments were conducted in a special insulated apparatus which provided a 77.3 cm^2 heat-transfer ar (i.e., cryogen-water interface area). Data include mass-vaporization/ time curve, vaporization rate curves, and approximate heat-transfer rates for the experimental conditions.

This study provides important background for studies evaluating hazards due to vapor dispersion from spills of cryogens on water. It is supplemented by a second study by the same authors and title, Part Light Hydrocarbon Mixtures.

Drake, Elisabeth M., Ayodeji A. Jeje, and Robert C. Reid, "Trans Boiling of Liquefied Cryogens on a Water Surface," Part II. Light Hydr carbon Mixtures, Int. J. Heat Mass Transfer, 18, 1369-1375, (1974).

Reviews related studies and presents results from experimental studies of transient boiling rates of synthetic binary mixtures of methane with ethane, propane, and n- and iso-butane spilled on water. Experiments were conducted in a special insulated apparatus which provided a 77.3 cm heat-transfer (cryogen to water) surface. Data ar presented as mass boiled as a function of time.

This study with Part I of the same title provides important back ground for studies evaluating hazards due to vapor dispersion from spills of cryogens on water.

Gas Processors Association, "LP-Gas Loading Practices Manual, Tulsa, OK, (1974).

Presents safety practices and procedures pertaining to loading and unloading of LPG from tank trucks, tank cars, ships, and barges. The bibliography lists twenty-one national codes pertaining, at least in part, to LPG transfers.

Gas Processors Association, "Liquefied Petroleum Gas Specificat and Test Methods," Tulsa, OK (1977).

The GPA recommended procedures for testing and specifying LPG a presented. Most of the tests listed are ASTM tests.

Gas Processors Association, "Method for the Underground Storage o
Natural Gas Liquids," GPA 8175-77, Tulsa, OK, (1977).

The GPA Standard for designing and constructing solution mined an
mechanically mined underground storage chambers for natural gas liquids
is presented.

Gas Processors Association, "Safe Practices for Loading LP-Gas In
Tank Trucks, as Recommended by Natural Gas Processors Association,"
Rev. (January 1966), (posters).

A listing of procedures to be followed for loading LPG into tank
trucks.

Gas Processors Association, "Standard Table of Physical Constants
of Paraffin Hydrocarbons and Other Components of Natural Gas," GPA 2145
Tulsa, OK, (1977).

A table of physical constants for common components of natural
gas is presented.

Gas Processors Association, "United States LP-Gas Import Terminal
1977," Tulsa, OK, (1977).

A compilation of data regarding U. S. terminal facilities with
the capability of receiving imported LPG is presented. Data includes
terminal locations, ship restrictions, type and capacity of unloading
system, storage capacity, etc.

Gunn, Robert D., "Natural Gas Liquids: Prediction of Vapor-
Liquid Equilibria for Process Design," 52nd Annual NGPA Convention,
pp. 5-9, (1973).

A computer program for calculating multicomponent phase equilibr
at cryogenic temperatures is discussed. No safety aspects.

Halliburton, W. A., Jr., "Low Temperature Gas Processing Operati
47th Annual NGPA Convention, pp. 128-133, (1968).

How to "make" LPG. Operation of a cryogenic-type gas processing
plant for recovering propane as LPG.

Henn, A. E., and J. G. Hicks, "Liquefied Gas Carriers--Statistica
nalysis of Ambient Design Temperatures for the United States," Gastech
NG/LPG Conference, New York, (October 5-8, 1976).

Provides temperature data for liquefied gas tanker hull design
strength) or certification for service.

Herrin, J. P., "Industry's First Successful High Propane Recovery
lant Using Expansion Turbines for Deep Refrigeration," 45th Annual
GPA Convention, pp. 97-101, (1966).

Discusses a new plant/process for recovering propane from natural
as. No safety aspects.

Horton, E. T., and John W. Lesch, "Design Features of Natural Gas
iquids Import Terminals," 57th Annual GPA Convention, pp. 202-206 (197

A general discussion of the many elements to be considered in de-
igning an LPG import terminal is presented. Includes a limited
escription of the general process steps used at one terminal, emphasiz
pecific capacities and daily throughput for tankers, pipelines, and
torage. Discusses only a terminal that uses salt-dome storage, heats
he gas liquid at the terminal to eliminate long runs of cryogenic
iping, and stores liquids in salt domes at temperatures no less than 3
ncludes discussion of receiving several gas liquids simultaneously.

Horton, John T., "Refrigerated Storage of LP-Gas," 41st Annual
GPA Convention, pp. 36-39, (1962).

Discusses the construction and economic aspects of steel refriger
PG containers. Includes a brief discussion of a weld failure and crac
n an LPG tank.

Hunt, J. W., "Special Considerations Related to Large-Scale Re-
frigerated LNG/LPG Custody Transfer Measurements," Journal of the
Institute of Petroleum, 58, (561), 158-163, (May 1972).

Possible sources of error in measuring the total volume of LNG/L
eing transferred from seller to buyer are discussed. The factors con-
sidered include heat input, liquid density, temperature and compositio
and instrumentation.

The Institution of Gas Engineers, "Safety Recommendations, IGE/S
Liquefied Petroleum Gases," Communication 762, London, (1968).

(Continued).

Provides reommendations for the safe storing, handling, and transp of liquefied petroleum gas. Contents cover the following general topics storage at refineries and bulk plants; industrial, commercial and domest storage; portable container filling; transport. Essentially a British version of NFPA 58.

Jones, Fred A., and Bruce L. Kline, "Conservation of Utilities in Design and Operation of Natural Gas Plants," 53rd Annual GPA Convention, pp. 149-158, (1974).

Details methods for conserving energy in the operation of natural gas plants.

Jordan, Charles H., "Recent Development in Cryogenic Materials anc Equipment," 46th Annual NGPA Convention, pp. 76-80, (1967).

A very general discussion of materials of construction and equipme suitable for cryogenic service. Not specific enough to be of practical use for hazard studies.

Kamata, Isao, et al., "Experimental Studies on Insulation Efficier on an Experimental LNG Carrier and a LPG Carrier," Hitachi Zosen Tech. Rev., 38, (1), 9-18, (March 1977).

Performance test of polyurethane foam insulation. Experiments and theory agreed on overall thermal conductivity.

Kaufman, C. Chris, "Microprocessor Eases LP-Gas Storage," Oil Gas 75, (46), 88-91, (November 7, 1977).

Shows flow loops, metering points and logic for product and flow control system in LP salt-cavern storage system and pipeline. Not highly relvant to safety study.

Kicks, B. J., "Natural Gas Storage in Refrigerated LPG," Gas Worl and Gas Journal, 182, (4706), 506-507, (September 1977).

A method for storing natural gas by absorbing it in LPG is presented. At high pressure and low temperature conditions (e.g. -40°C an 40 bar), more gas can be stored in solution in LPG than can be stored in the same geometrical volume using conventional dry gas storage at th same pressure and temperature.

Klehm, Julius J., Jr., and John E. Singletary, "Design and Start
of the Sea Robin Gas Processing Plant," 53rd Annual GPA Convention, pp. 167-170, (1974).

Discusses the design and startup of an offshore, cryogenic gas processing plant. No safety aspects.

Kymer, R. F., "Aftercoolers, Storage Tanks, and Lines," 42nd Annual NGPA Convention, pp. 7-8, (1963).

Concerned with air compressors--no safety aspects.

Lakey, R. J., "The IMCO Code for Gas Tankers. A Review of the Finalized Code," Gastech 75, LNG & LPG Technology Congress Proceeding
Paris, 65-69, (September 30 - October 3, 1973).

Presents an outline of the IMCO Code for the construction and equipment of ships carrying liquefied gases in bulk. Contained in a list of the products covered by the code are butane, propane, and buta
propane mixtures (LPG).

Leach, David M., "World's First Totally Offshore NGL Facility - Java Sea, Indonesia," 54th Annual GPA Convention, pp. 166-170, (1975)

An offshore facility for recovery, storage, and export of NGL i
described. NGL recovery unit and refrigerated LPG storage barge (pre
stressed concrete hull with steel tanks) are described in detail.

Leclercq, J., and H. Baker, "Cargo Leak Detection Systems for Cryogenic Tankers," Gastech 75, LNG & LPG Technology Congress Proceedings, Paris, 185-191, (September 30 - October 3, 1973).

A review of the sections of the IMCO code that pertain to cargo leak detection systems is given. The principles of operation and advantages/disadvantages of the various methods available for detecti
the presence of a flammable gas are discussed. Sampling system desig
operation, and maintenance are also discussed.

McNall, Fred, "Recommended Maintenance Procedures," 42nd Annual

45. Miller, E. J., and K. W. Stevenson, "Design Technolog
Propane Compressors," 46th Annual NGPA Convention, pp. 84-8

Discussion limited to propane compressor design for r
service. Not pertinent to study of hazards.

46. Montgomery, C. F., "Changing Modes of Transportation
43rd Annual NGPA Convention, pp. 43-46, (1964).

A historical look at changes in modes of LPG transpor

47. National Fire Protection Association, "Storage and Ha
Liquefied Petroleum Gases, 1974," NFPA No. 58, Boston, MA (

NFPA standards for equipment, appliances, installatio
portation, and storage of LPG. The basic area of applicati
residential and small commerical uses. It does not apply t
installations.

48. National Science Foundation, "Confined Boiling Rates
fied Petroleum Gas on Water," Robert C. Reid and Kenneth A
Mass., Massachusetts Institute of Technology, (1978), (HCP/

Presents results of experimental "spills of LPG, prop
ethylene, and n-butane on water in a specialized experimen
having a 191 cm^2 heat-transfer surface. Two tests with pro
and propane on agar gel were also run. Results are presen
vaporized as a function of time.

A basic science study applicable to study of LPG spil
vaporization as input to dispersion models.

49. Noeltner, Robert H., Jr., and William J. Martinec, "
Instrumentation and Control System for Floating LPG Termin
Offshore Technol. Conf. 7th Annual Proc., Houston, TX (May
V. III, Paper OTC 2426, p. 829-838.

A description of the instrumentation and control sys
first floating LPG terminal is presented. The terminal is
barge and will be located in the Java Sea off Indonesia.
discussion of the instrumentation is given, including the
and instrument redundancy. The system utilizes capacitanc
sensors, LVDT type pressure sensors, an attitude sensor, c
cessing computer and a complete console which provides dis
controls and alarm annunciators.

Pinson, J. A., "A Review of Gasoline Plant Property Losses," 49th Annual NGPA Convention, pp. 163-164, (1970).

A general discussion of failure modes and effects in gasoline plants, emphasizing fire events. Although discussion is quite genera some information is useful as generic data. Provides a tabulation of dollar losses from 96 events during the period 1959-1968, but information is not usable for failure-rate data.

Poten & Partners, "Liquefied Gas Ship Safety, the Historical Record, 1964-1977," New York, (1978).

Report on factual history of gas ship safety, from 1964 - 1977, collected from marine accident reports and other casualty reports submitted to insurance carriers. Includes statistical summary of the da

World Fleet of 171 ships larger than 5000 m^3 (1964 - 1977)

a) delivered 16,000 cargoes

b) accumulated 960 ship-years of service

c) accounted for only 28 serious incidents involving potential hazards at import terminals

c) of the 28 incidents, only one involved leakage of cargo (leaky valve) and none apparently involved ignition of the main cargo

The collision of the Yuyo Maru and the Pacific Aries is not included as a cargo fire because "it is not clear whether the LPG tanks eventually failed." The LPG tanks did vent and the cargo did burn.

Rabe, Walter M., "Refrigerated LP-Gas Tanker Operation," 53rd Annual GPA Convention, pp. 138-142, (1974).

The principles of operation of a typical LPG tank ship are presented. Lists of the LPG tank ship fleet and U. S. LPG marine terminals are given along with a discussion of the future demand for more LPG tankers.

Rasch, J. M. B., "Petter," "Design Features and Availability of Liquefied Gas Carriers," 57th Annual GPA Convention, pp. 195-201,

A review of the various types of tanks used to contain LPG abo LPG tank ships is presented. Those portions of the IMCO code and US regulations that pertain to tank design are discussed.

Reid, Robert A., "Design and Operation of Refrigerated LP-Gas Terminals and Requirements for New Terminals," 53rd Annual GPA Convention, pp. 143-144, (1974).

The design and operation of various U. S. LPG marine terminals are discussed. An increase in the number of terminals needed is predicted.

Reid, R. A., "Safety Considerations in the Design and Operation of a Refrigerated LP-Gas Marine Terminal," Proceedings American Petroleu Institute, Section III, Refining, v. 54, 1975 for Meeting, Chicago, IL, p. 471-483, (May 12-15, 1975).

General discussion of plant, layout, operations, and safety at Petrolane's marine import terminal, San Pedro, California.

Reid, Robert C., and Kenneth A. Smith, "Behavior of LPG on Water," Hydrocarbon Processing, 57, (4), p. 117-121, (April 1978).

Heat transfer model of boiling rate for LPG, with a growing ice shield, described. Adding small quantities of ethane or n-butane to the propane had essentially no effect on the heat flux curves. Thus, the boiling of LPG may be modeled satisfactorily by using pure propane. Ethane - a moving boundary model might be applicable in the same manner as employed for propane spills. In theory, after an ice shield forms, the heat transfer rate is significantly above that of LPG; although in the very short period following a spill, LPG boils at a rate very much faster than ethane. Ethylene - model same as LPG and ethane. n-butane the rate of boiling is far less than other liquefied hydrocarbons studi

Robinson, H. S., "An Underwriter's Viewpoint on Gasoline Plants--They Can Burn," 49th Annual NGPA Convention, pp. 161-162, (1970).

Provides Oil Insurance Association's minimum fire protection recommendations for a well-protected gasoline plant. Includes general mention of serious fire protection design deficiencies observed by underwriters. Useful only as general background.

Ryburn, John E., "Design Considerations and Start-up Problems in the Wasson Plant Low Temperature Process," 49th Annual GPA Conventio pp. 130-135, (1969).

The operation of a gas processing plant for the recovery of ethan and propane is described. Measures taken to reduce the risk of fire or explosion within the plant are discussed.

Schneider, Alan L., "Liquefied Natural Gas Safety Research Overvi
Paper, 1978 American Gas Association - Cryogenic Society of America LNG
Terminal & Safety Symposium, San Diego, CA, (October 12-13, 1978).

A significant review of 105 research papers on LNG safety researc
This is an important resource book for study of LPG safety because of
the transferable applicability of results for LNG to LPG. Necessarily
limited in detail, but provides adequate information to allow informed
selection from the cited papers.

Taher, Abdulhady H., "Supply/Marketing of Natural-Gas Liquids," 5
Proceedings Annual Convention Gas Processors Association Technical Pape
Dallas, TX (March 21-23, 1977). Published by Gas Processors Associatio
Tulsa, OK, p. 134-135, (1977).

This report concerns the exporting of propane, butane, and natura
gasoline from Saudi Arabia and gives predictions of the volumes to be
exported by 1985 and predicts U. S. imports for 1985.

Tavana, M., "Iranian Gas Production and LP-Gas Manufacturing,"
54th Annual GPA Convention, pp. 160-165, (1975).

Describes Iran's gas reserves, LNG and LPG production and tabulat
Iran's LPG production, 1970-1974.

Thomas, William du Barry, and Alfred H. Schwendtner, "LNG Carrier
The Current State of the Art," The Society of Naval Architects and Mar
Engineers. Advanced copy of paper to be presented at the annual meeti
New York, November 11-12, 1971. (Oceanology, March 1972, 19-24).

Describes basic design of LNG ships. The only mention of LPG is
that some of the ships have reliquefaction equipment installed that
enables them to carry other cryogenic cargoes.

U. S. Department of Energy, "Unconfined Boiling and Spreading
Rates of Liquefied Petroleum Gas (LPG) Spilled on Water," Renewed
Proposal. Robert C. Reid and Kenneth A. Smith, Massachusetts Institut
of Technology, (1978).

A literature review on contact boiling between two immiscible li
heat transfer to boiling liquid mixtures, and boiling of cryogenic liq
on solids and water is presented. Data from some LNG spills on water
compared to the total time to evaporate and maximum pool diameter as c
culated by three different mathematical models; agreement was not good
The author's one-dimensional boiling and spreading model is then discu

3. (Continued).

in detail. A proposed experimental program for studying simultaneous boiling and spreading of LPG spills on water is described. Prelimina experiments with the proposed test apparatus showed that ice formed o the area of the water surface immediately upon contact with LPG; this is contrary to previous LNG tests where no ice formation was observed

4. U. S. Department of Transportation, "LNG/LPG Contingency Plan, Captain of the Port, Rhode Island," United States Coast Guard, (1975)

Contains general regulations and requirements of the port, and a hazard assessment using the Chemical Hazards Response Information System (CHRIS).

5. Wheatley, W. H., "Safety Considerations in the Design and Opera of Sour Gas Processing Plants," 49th Annual GPA Convention, pp. 156-1 (1969).

Design and operational considerations affecting safety in sour processing plants are discussed. Major emphasis is on hydrogen sulfi

6. Williams, Robert A., and Robert L. Blanchard, "LPG Measurement and Custody Transfer," 57th Annual Convention, pp. 212-213, (1978).

LPG custody transfer systems based on shipboard instrumentation for measuring the mass of liquid and gas in the ship's tanks are described. The accuracy of measurement is given for various types of measuring devices.

REPORT U

Critical Review and Assessment of Environmental and Safety Problems in Hydrogen Energy System

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TABLE OF CONTENTS

Although no large-scale intrusion of hydrogen into the energy market ninent, there is good reason to believe the use of hydrogen will continu increase. There is also sufficient current interest in hydrogen as an ergy material, to justify an independent examination of the safety and vironmental consequences of its use.

This project was originally intended to assess the safety of hydroger pments. Subsequently, it grew into an assessment of the safety and env ntal aspects of the production, storage, shipment, and end-use of hydrog this reason, the safety problems anticipated in the shipment hydrogen re studied first. The most probable modes of shipment were considered t the transmission of gas by pipeline and the bulk shipment of cryogenic quid hydrogen. It was also necessary to address the problems of hydroge orittlement and the existing rules, codes, and regulations controlling t ipment of hydrogen.

The investigations of hydrogen embrittlement and rules and regulatior e essentially complete. The considerations of the shipment of hydrogen ther as a gas or as a liquid will be completed in FY-79. The assessment the environmental effects of hydrogen was begun in FY-78 and will be co FY-79.

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1. INTRODUCTION

The environmental and safety problems anticipated in the use of hy
en energy carriers are being reviewed at the Los Alamos Scientific Labor
LASL). The work done during FY 1978 has been discussed in an annual rep
ow in the editing phases. A previous annual report (LA-7405-PR) covers
er work.

The advantages of hydrogen as a fuel stem mainly from its extremel
ide-spread availability if produced from water, the relatively benign ch
er of the environmental aspects of its use as a fuel, its potentially hi
fficiency in almost every application proposed so far, and its compatibi
ith existing energy systems.

The disadvantages of the introduction of hydrogen as a fuel stem f
actors such as the economic disadvantage of competing with existing foss
uels along with the existing investment in equipment for their productio
istribution and use, the weight and/or volume of storage, and the concer
afety. The environmental acceptability of the use of hydrogen is a real
dvantage in spite of the pollution potential of the prime energy necess
or the hydrogen production. Perhaps the most serious disadvantage of th
f hydrogen, which it shares with any synthetic fuel, is that hydrogen is
n energy source and will take more energy for its production than will
ecovered in its use.

rvice stem from concerns about material compatibility and leakage. The
terial compatibility problem results from hydrogen embrittlement. Althou
ch pipeline is an individual case and must be individually studied, Depar
ent of Energy (DOE)funded work, being done at the Sandia Livermore Laborat
LL), indicates that the pipe wall material will probably be satisfactory
drogen service if the working pressure of the pipeline is derated to perh
% of the original working pressure. Welds are also a problem. Again, th
idence generally indicates that good welds will perform similarly to the
pe wall material; however, if there is cold cracking in the weld, hydroge
y cause failure where this would not have been the case in natural gas se
ice.

In present natural gas systems, leakage losses have been estimated t
ount to as much as 10% of total use. There is frequently a concern about
e fact that hydrogen can be expected to leak faster than natural gas. Ho
er, although the leakage can be expected to increase by a factor of about
ree, the energy density in the leakage gas is less than that of methane a
a factor of about three, so that the total energy release is about the s
that of natural gas. Therefore, for outdoor leaks there would appear to
great difference in the consequences. In fact, there are reasons to cre
drogen with a safety advantage in this case. The higher diffusivity and
oyant velocity of hydrogen will result in faster dissipation of combustib
drogen mixtures compared to natural gas. In the case of leakage into a c
ined area, however, hydrogen will reach explosive proportions approximate
ur times faster than natural gas.

Another matter of concern is evaluation of the fire hazards or damag
tential from hydrogen fires compared with those from natural gas fires.
rcentage of thermal energy radiated from flame to surroundings is similar
r hydrogen and methane. However, because the hydrogen radiates outside t
sible (in the infared) portion of the spectrum, the hazard from the hydro
re will be less than from the equivalent natural gas fire because of abso
ion in the air by water vapor.

ves Committee on Science and Technology. It was concluded at this work
at hydrogen fuel will not survive in the marketplace unless certain con
ons are fulfilled. First, we must obtain the necessary prime energy an
cond, one of the following conditions must obtain:

- A national commitment to decrease petroleum imports for econ or security reasons,
- The exhausting of the fluid fossil fuels,
- A requirement to reduce carbon dioxide emissions, and
- A necessity to impose much tighter pollution controls.

Another conclusion of the workshop was that it was important to kee
hydrogen energy option open by starting some demonstration projects th
ld illustrate the feasibility of the use of hydrogen as an energy carri
cific suggestions were hydrogen-fueled aircraft, the addition of hydrog
natural gas, and fleet vehicles fueled with hydrogen.

Although significant intrusion of hydrogen into the energy system w
resent a large increase in the production of hydrogen, the US does alr
e a substantial hydrogen technology. Approximately two trillion cubic
hydrogen are produced annually, and although almost all of this is use
mical processes and on the premises where it is produced, there is a
l-developed hydrogen transportation technology. Hydrogen has been shi
a gas by pipeline and high-pressure cylinders for about 60 years, and
uid for over 25 years. Present shipments of liquid hydrogen by rail t
have already reached the stage where approximately one rail tank car
ves Los Angeles for Chicago every day.

arket seems imminent, there is sufficient interest in its use to justify
ndependent examination of the safety and environmental consequences of i
se.

This project was originally intended to assess the safety of the sh
ent of hydrogen. Subsequently, it grew into an assessment of the safety
nvironmental aspects of the production, storage, shipment, and end-use o
ydrogen. For this reason, we first studied the safety problems anticipa
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ing the shipment of hydrogen.

The investigations of hydrogen embrittlement and rules and regulat
re essentially complete. The considerations of the shipment of hydrogen
ither as a gas or as a liquid will be completed in FY-79. The assessmen
he environmental effects of hydrogen was begun in FY-78 and will be cont
n FY-79.

2. TRANSMISSION OF HYDROGEN GAS BY PIPELINES

Of the various possible modes of transporting hydrogen, the transm
ion of hydrogen gas through pipelines is one of the most likely for earl
mplementation. One application that could be implemented quickly is the
ddition of hydrogen to natural gas to extend the existing natural gas su
ly. While the exact amount of hydrogen that could be added is not well
nown, it appears that in amounts up to about 10% by volume hydrogen, the
ill be no noticeable effect in the combustion properties other than the
light lowering of BTU content of the gas mixture. There would appear to
o safety problem to impede the addition of hydrogen to existing natural
ystems. Whether this addition would be made in the transmission system
he distribution system would, of course, depend on the location of the h
en source with respect to the use point.

dicated to the transmission of hydrogen. One suggestion has been the
rsion of existing natural gas lines to hydrogen service. The natural
ansmission system consists of gathering lines, transmission lines (~26
es), compressor stations, storage facilities, and the associated moni
l safety systems necessary for operation. The transmission network ge
y originates in the southwest and delivers gas to the east and west c
l to the midwest. Storage is either underground or as liquefied natur
NG) to be vaporized during peak demand periods. The existing natural
ansmission system contains a wide variety of conditions and materials
use of the age of the system. Generally, the pipe materials are "mild
eels" with 0.15-0.39% carbon and 0.5-1.0% manganese. The lines also h
rge number of welds. Typical pipeline sections consist of large diame
--48 inches) pipe with factory-made longitudinal seam welds. The sect
e then field welded at the girth.

Even though the economics of using existing natural gas transmiss
stems is favorable, the choice may not be ideal for two reasons. Firs
pply of hydrogen probably will not be in the right place; and second,
isting pipelines are not optimized for hydrogen transmission. If the
n is to be produced from coal, there are a number of possible source l
ons, none of which is close to the present largest source of natural g
e next most likely energy source to produce hydrogen in the near term
clear power. In this case it might be more practical to locate the hy
oduction facility nearer the use point, again obviating the large-scal
existing natural gas pipelines. Also, the most promising solar energ
rces are not conveniently located to serve existing pipelines.

Optimization for hydrogen service is also important and not much
ing can be done in converting existing pipelines to hydrogen service.
der to carry the same energy flow in an existing pipeline, much larger
essor power consumption will be required. Although pressure dependent
wer increase is typically about a factor of five.

fireballs. Fireballs can vary in character from a low order turbulent
gration in a premixed fuel/air cloud to pure fuel vapor cloud that burn
its edges as a turbulent diffusion flame. Hydrogen fireballs can pose
ous burn hazards with the majority of the radiation in the infrared reg
the spectrum. Third-degree burns from a large hydrogen fireball (10^7 t
10^8 kg) could occur out to distances of several kilometers from its cen
We intend to investigate the hydrogen fireball model. This will be don
the next year of this project at China Lake, California.

Concerns about the use of hydrogen at high pressures and the pos
bility of the ignition of expanding hydrogen due to the Joule-Thompson
are unjustified. If a gas is expanded from an initial temperature abov
inversion temperature (202 K for hydrogen), a temperature increase in t
will result. For pressure ratios that will be used in a hydrogen syste
temperature rise on free expansion is only around 10^{o} to 20^{o}C or less.

A more justified concern is other sources of ignition such as sh
ignition of hydrogen. Under certain geometrical conditions, a shock wa
form when hydrogen is vented. The temperature in the wave can exceed t
auto-ignition temperature of hydrogen, causing hydrogen to ignite. The
cal and experimental investigations should be carried out to determine
parameters of this reaction.

The use of pipelines specifically designed for hydrogen service
nates the problems encountered in the conversion of existing natural ga
lines. The construction of such lines is more expensive and to make th
economically feasible, requires the need for large quantities of hydrog
be supplied to definite locations for longer periods of time. However,
capability of safely shipping hydrogen by this means has been, and cont
to be demonstrated, on a small scale. A 2.5-cm (1-inch) line at LASL w
at pressures up to 17 MPa (2 500 psi) for 6 years.

and Chemicals Inc., is 27 km (17 miles) long and has diameters of 10
(4 and 8 inches). In Germany a hydrogen transmission line in curren
ce is 209 km (130 miles) long, and has diameters of 15 to 30 cm (6 to
s). Although these pipelines are operated at low pressure and the di
and the quantities of gas are small compared to natural gas systems,
monstrate that it is possible to ship hydrogen safely by pipeline.

For new systems it will be necessary to optimize parameters for hyd
ransmission. This will probably include higher pressures (perhaps 12
800 psi) and lower pressure ratios for compressors (more like 1.1 to
r than the 1.3 to 1 usually used in natural gas service). These esti
are closely dependent on the cost of the hydrogen used to fuel the
e to drive the compressors. Selection of materials will continue to
tant. Good quality control in welding and better leak detection will
red in line construction. And a continuing research effort in the in
ion of hydrogen embrittlement is advisable.

3. SHIPMENT OF HYDROGEN AS A LIQUID

Pipeline shipment of hydrogen is practical only where a large deman
r and an established source point can be expected to remain stable fo
ded period of time. Because of the requirements of the US space prog
arge quantities of liquid hydrogen (LH_2), a mature technology for the
ction and transport of LH_2 was developed. Despite the wide fluctu-
s in the requirements of the government programs, this technology has
ved and now serves a wide-spread network of consumers with LH_2.

This method of distribution of hydrogen is not without its disadvan
. First, there is the energy required for liquefaction. Theoretical
would amount to 10% of the energy of combustion of the hydrogen. How
even the largest liquefiers only attain about 35% of this efficiency

efrigeration available.

Once liquefied, the LH_2 presents an energy carrier that exhibits a
f the properties that make hydrogen gas difficult to handle and, in addi
s a cryogen, also has high volatility and low temperature. The high vol
ility can cause unwanted pressure build-up if containers are not proper
ented. The low temperature can cause condensation of air to a solid (wh
an plug vents) or, because the condensed air is enriched in oxygen, can
xplosive hazards when the condensate falls on combustible substances suc
sphalt. The low temperature can also cause dimension changes or cold-
mbrittlement in structural elements, creating a secondary hazard. There
lso the possibility of cold damage (frost bite) to human tissue; however
his phenomenon has not caused much trouble throughout the history of LH_2
andling. The high volatility and unavoidable heat leak into the storage
ainer may require some venting of boil-off gas and consequent loss of pr

In spite of this list of difficulties the shipment of LH_2 by highw
railer, rail tank car, and barge has been shown to be both safe and econ
al. In comparison to the largest gaseous hydrogen tube-trailer, which c
ransport 3 800 m^3 (135 000 standard cubic feet (SCF)), a 49 000 ℓ (13 00
al) LH_2 highway trailer can carry the equivalent of 42 000 m^3 (1 500 000
CF). For this reason, where pipelines do not already exist, hydrogen is
rimarily transported to all but the smallest users as a liquid, regardle
he final use.

Road trailers of 30 000 and 49 000 ℓ (8 000 and 13 000 gal) capaci
ave been in routine service for more than a decade. These units have
oil-off losses of only a few tenths of a per cent per day so that it is
ible to close the vent valve and deliver LH_2 to any part of the continen
S without venting any hydrogen. This method of shipment has been used i
elivering many millions of gallons to numerous users in many parts of th

ntioned highway trailers for distribution to a large part of the easter . The largest LH_2 transport capability is in 950 000 ℓ (250 000 gal) vars mounted on seagoing barges.

Although the largest liquid hydrogen production facilities in oper e at about the 60-ton/day size, studies of much larger production facil ve been made. As early as 1968, Hallett of Air Products evaluated prod on facilities of a capacity up to 2 500 ton/day to support worldwide de nt of hydrogen-fueled hypersonic transport aircraft. Baker of Linde mo cently evaluated facility sizes up to 2 500 ton/day, pointing out that y of scale considerations to lead about a 250 ton/day "module" as being propriate for a single liquefaction train. The step-up in size over th rgest unit to date (60 ton/day) is notable, but this would seem to pose rticular problem or technical barrier.

Application studies for locating hydrogen liquefiers near major ai rts to fuel projected wide-body commercial aircraft fleets were carried r the National Aeronautical and Space Administration (NASA) by study te d by Lockheed and Boeing in 1976. In evaluating such a facility for Ch go's O'Hare Field, Boeing determined that an 800-ton/day liquefaction f y would be appropriate.

The bulk shipment of hydrogen as LH_2 is an accomplished and succes l technology that shows every sign of growing. We believe that the lar ale expansion of hydrogen into any facet of the energy system will invo creased shipment of hydrogen as LH_2.

The safety of this type of operation has been demonstrated. Also, ve performed a preliminary analysis of the risk of highway LH_2 transpo wever, the data are too scarce for it to be reliable. To date we have port of any transportation accident in which there were fatalities or s s injuries that could be attributed to the cargo being LH_2. As more da e gathered better risk analyses can be made.

spersion and distribution of hydrogen in the vapor cloud after a serious nk rupture. Small-scale spill tests have been performed by Arthur D. Lit c. and by the US Bureau of Mines, but data from larger and more instrumen sts are required. The NASA is beginning a better instrumented set of exp ents to be conducted at the Naval Weapons Center at China Lake, CA. The sts will be valuable, but will need to be followed by even larger tests. e collaborating with NASA in planning the China Lake tests. We have con- ibuted some of the equipment and will receive the test results when they ailable.

4. HYDROGEN EMBRITTLEMENT

Hydrogen embrittlement is the deleterious effect of hydrogen on the chanical properties of structural materials. These adverse effects have een recognized for over a century, however, the detailed or microscopic ture of this phenomenon is still not completely understood. As early as 940's many hundreds of papers had been written on this subject and now ref ences on this topic number in the thousands.

Hydrogen affects metals by three different mechanisms: hydrogen action embrittlement, hydrogen internal embrittlement, and hydrogen envir nt embrittlement. The first of these usually occurs at elevated tempera- res, is chemical in nature, and is the best understood. The last two are ysical in nature and are most serious near ambient temperature. In react brittlement hydrogen is absorbed either during processing or during servi d the absorbed hydrogen reacts with either the metal itself or some alloy purity component. When the reaction is with the base metal (or one of th jor alloying elements) hydride embrittlement may take place.

Hydrogen reaction with minor alloy and impurity elements is also wel derstood, particularly in the cases of hydrogen reaction with carbon in eels and with oxygen in copper and/or silver. The reaction product (CH_4

ter, for example), it is difficult to contain the insoluble gaseous pro t. Bubbles nucleate and grow at internal boundaries; when the bubbles critical size and distribution, the mechanical properties of the alloy verely degraded. Considerable work is needed to determine susceptibili is form of hydrogen damage before structural materials are considered f e very severe environments typical of coal gasification or other hydrog oduction processes.

Internal hydrogen embrittlement is caused by absorbed hydrogen. I nerally accepted that such embrittlement is promoted by localized, high drogen concentrations. Such concentrations frequently develop from str hanced diffusion of absorbed hydrogen in the form of high-pressure gas es at lattice defects. This form of embrittlement is promoted by high plied (or residual) stresses, sharp notches, and high material yield rengths. This process manifests itself in crack formations requiring a cubation period. It is reversible in the sense that if cracks have not rmed and the hydrogen is removed, there is no embrittlement. Perhaps t st insidious effect of internal hydrogen embrittlement is that it can velop because of hydrogen absorbed during any stage of manufacture and a component, the part need not be further exposed to hydrogen until th me of failure.

Environmental hydrogen embrittlement was only widely recognized in te 1950's or early 1960's. This form of damage is most often observed astically deformed metals and alloys while in a high-pressure hydrogen vironment. Frequently, such deformations are accompanied by surface cr g, ductility losses, and decreases in the true fracture stress. Few en ering structures are designed to undergo significant plastic deformatio ring service. Although there have been no one-to-one comparisons betwe st results and design, the observation of environmental hydrogen embrit nt has at least one very important implication. When plastic deformati drogen environments occurs, the metal's serviceability is shortened. tigue and creep represent two common types of plastic deformation failu

Unfortunately, hydrogen embrittlement is apparently unknown to many workers in the field. This is probably due to the excellent safety record of the distribution of gaseous hydrogen in mild steel cylinders over a period of perhaps 60 years. Inquiries to foreign countries have revealed that the safety record in France is also excellent, however, this is not the case in Germany where a number of hydrogen tube-trailer failures have been reported (perhaps as many as 70). The failures in Germany have been attributed to improper material selection (caused by shortages) and aggravated by the vibration of transport and numerous pressure cycles. Where the safety record is excellent, this has been attributed to very conservative design.

The majority of US research projects studying hydrogen in metals is funded by the Department of Energy (DOE), the Department of Transportation, the NASA, and the National Science Foundation at various university, industrial, and national laboratories. Hydrogen effects on a wide variety of metals have been studied at Rocketdyne Division, Rockwell Science Foundation. Work at that site is perhaps the most extensive high-pressure hydrogen work in the country. SLL also has a hydrogen program directed toward determination of the feasibility of using the current natural gas pipeline system for transport and distribution of gaseous hydrogen. This program includes a test hydrogen pipeline. Hydrogen in metals studies are also conducted under the auspices of the DOE at the Savannah River Laboratory and at the Pratt-Whitney Aircraft Company. The Virginia Polytechnic Institute research is under contract to study specifically the role of stress state in high-pressure hydrogen embrittlement processes.

The mechanism of hydrogen embrittlement is being studied at numerous locations. The NASA Ames Research Laboratory has an extensive investigation of hydrogen embrittlement, and research at the Carnegie Mellon University is investigating the role of metallurgical variables in the embrittlement process; Brown University is studying hydrogen effects on interface cohesion; Columbia University is modeling hydrogen transport by dislocation; and the University of Notre Dame is studying hydrogen-defect interactions. Hydrogen diffusion is studied at numerous university and national laboratories. Hydrogen embrittlement research is performed in several foreign countries, particularly in France and West Germany.

ressures may be encountered and it will be necessary to use materials t
re relatively inexpensive and readily available. For this to occur saf
t is necessary to continue the ongoing research that is leading to an u
tanding of the problem. Tests should be conducted under realistic and
rolled conditions of hydrogen exposure time, purity, pressure, system t
ture, metallurgical condition of test specimen, and the stress state an
oading rate of the specimen. A method of accelerated testing is necess
s also the development of scaling factors.

5. CODES, STANDARDS, AND REGULATIONS

In the introduction of hydrogen into any aspect of the energy sys
he environmental and safety aspects are of major importance. Any propo
se must be accomplished without significantly increased risk to the publ
r without causing additional safety problems. Also the increased use m
e accomplished without jeopardizing the further development of the
echnology. The absence of regulations can, in itself, sometimes be an
mpediment to the use of a new technology. On the other hand, if a new
echnology is inhibited unreasonably, we may miss a chance to effect a
omprehensive improvement for society; therefore, the goal must be to
ecrease risk, but no necessarily to zero, because in most cases that is
mpossible. Along with this it is always necessary to eliminate irrele-
ant or outmoded requirements. Unnecessary safety rules restrict operat
nd may result in loss of respect for other rules that are valid, which
ould lead to other hazards.

To carry out a good, comprehensive safety program, a continuing
lti-faceted effort is required. First, it is necessary to understand th
ndamental physical processes that could take place in any credible mish
d the possible consequences. These processes must then be taken into
count in the design of equipment and in the determination of operating
ocedures. Next, this knowledge must be used in the writing of the nece
gulations. Finally, a continuing effort is required in the updating of
ocedures and the training and monitoring of personnel.

oped by organizations (or groups representing such organizations) f
own needs. Examples are the NASA and the Los Alamos Scientific La
These organizations assign technically qualified personnel (or comm
evaluate hazards and to develop information, rules, and guides to r
operational risks.

Codes and standards are consensus safety documents developed
profit trade associations, professional societies, or standards mak
testing bodies that serve industrial, commercial and public needs.
are the American National Standards Institute (ANSI) or the Nationa
Protection Agency. These bodies are empowered to include advisory
datory provisions that may be adopted by authorized regulatory age
Codes and standards are usually initiated, when a need arises, by m
these nationally recognized organizations. The efforts involve a r
available information from which the scope of the proposed code or
developed. A tentative version is usually published for review by
persons and organizations. The comments are evaluated, and, if ne
tentative standard or code is prepared. The authorizing committee
organization and subsequently a governing board both vote to accep
the code. Code writing is a lengthy procedure and can take years.
effort of the ANSI to prepare a cryogenic piping code has been in
over 7 years and is still continuing. It might also be mentioned
present no code exists for storage of cryogens in cryogenic storag
Although these vessels are almost always in capable and well-train
such a code should be written.

Regulations are directives by official bodies authorized to
safety requirements enforceable by political jurisdiction. On the
level, these include the United States Department of Transportatio
and the Occupational Health and Safety Act (OSHA). In addition to
agencies, state and local officials may also issue regulations. R
tions of other government agencies and of interested parties are a

on is given to oral arguments made by interested parties. When final r
tions are published, provisions are made for interested parties to peti
e officials to amend or repeal these regulations.

There are a number of specialized organizations recognized as auth
ies through which information can be disseminated. Some examples are:

- International Society of Fire Service Instructors
- International Association of Fire Chiefs
- National Fire Protection Association
- International Association of Firefighters

Most regulations originate with the federal government and are con
ined in the Code of Federal Regulations (CFR) where they are introduced
ganizations such as USDOT, OSHA, or the US Coast Guard. For example,
enty-six CFR's are identified that regulate the transport of hydrogen,
imarily by inference. Only a few of these specifically address hydroge
ansport; those referring to transport of liquid hydrogen discuss only s
cations for railway tank cars. States can also exercise this type of c
ol, but seldom do so. Many municipalities, however, control hydrogen b
ans of fire ordinances and by adopting codes.

This network, with input from professional bodies, trade and inter
oups, state and local jurisdictions, and federal directives, is somewha
ffuse and unorganized. Yet, it has proved adequate for the present qua
hydrogen use. It should also be sufficient for presently contemplated
monstration projects. As the public exposure increases (because of tra
rtation, proximity to inhabited areas, public visibility or interaction
l need more specific and inclusive organizational control.

reased hydrogen use was begun. Although the impact is generally favorabl he situation is not as favorable as is frequently expressed. Early state ents about hydrogen and the environment were glowing reports about hydrog otal lack of pollution. These claims were made only for the end-use of t ydrogen and ignored the extra energy necessary for hydrogen production. he end-use claims were not valid. The use of hydrogen fuel in internal c ustion engines results in no unburned hydrocarbons or carbon monoxide in xhaust. However, nitrogen oxides are formed. Some formation of hydrogen eroxide has also been reported; but this is not normally expected under esirable operating conditions. The nitrogen oxide production can also be ontrolled by proper selection of engine operating conditions and attempts eing made to learn ways essentially to eliminate this pollutant by cataly eduction with excess hydrogen to form nitrogen and water.

Nitrogen oxide pollution can also result from the combustion of hyd en in open flames. This unwanted reaction can be controlled by adjustmen uel-air mixture, or for some applications it is possible to perform the ydrogen oxidation catalytically at a sufficiently low temperature that no itrogen oxides are formed.

Although water is not usually considered a pollutant, there is one ituation where this assumption may be invalid. Hydrogen has been conside s the fuel for the advanced supersonic transport. Whether the water bein eleased in the stratosphere can be a problem will, of course, depend on t otal quantity and distribution of flights.

The major source of pollution resulting from the wide-spread use of ydrogen as a fuel is to be found in the extra generation of energy requir or its production. As mentioned previously, hydrogen is not a source of nergy, but rather is an energy-carrying medium. As with any synthetic fu ore energy will be required for its production than can be recovered in i

s for the ratio of source energy to hydrogen energy have ranged from t ive, depending on the efficiencies assumed and whether or not the hydr o be liquefied. For hydrogen produced from coal, we can consider the tive efficiencies for its production compared to other synthetic fuels comparison has been made more than once for hydrogen and methane, but conflicting results. Attempting to predict the extra energy required production is very sensitive to the assumptions made, thus it is diffi redict the environmental effect of hydrogen production. Presumably th ution can be better controlled more easily at the source; this fact, p more environmentally benign end-use of the hydrogen compared to hydroc fuels, do add up to an environmental advantage for hydrogen.

During this fiscal year we are studying the nitrogen oxide emission internal combustion engines and the process of removal of these oxide lytic conversion. We also will perform an environmental analysis of o ess for the thermochemical production of hydrogen from water and will studies on the environmental impact of hydrogen production from coal.

We are also modeling by computer the dispersion of a hydrogen clouc r a gas leak or liquid spill. Previous attempts to solve this problem not included the important effect of heat transfer to the cold vapor d resulting from a liquid spill. Tests are planned by the NASA to stu problem experimentally with LH_2 spills. These will be conducted at t l Weapons Center at China Lake this winter and should provide the nece experimental data to verify the calculations at least for a spill on e of a few thousand gallons. Although this task is safety rather than ronmentally-oriented, these calculations make use of computer codes loped for pollutant dispersion in the atmosphere.

During FY 1976 the continuing program is intended:

1. to complete the review and assessment of gaseous hydrogen shipment by pipeline (this will include a review of accidents in the transmission of natural gas for comparison with hydrogen service

2. to complete the review and assessment of the bulk transport of LH_2 (this will include a cooperative effort with NASA in the LH_2 spill tests to be performed at China Lake),

3. to study analytically the dispersion of hydrogen after a gas lea or liquid spill,

4. to study the catalytic reduction of nitrogen oxide emissions fro hydrogen fueled internal combustion engines,

5. to study the emissions from the production of hydrogen by the thermochemical splitting of water and by coal gasification,

6. to study the effect on explosive characteristics of the additio of hydrogen to methane, and

7. to prepare a summary of desirable safety and environmental research.

In the course of this investigation to date, we have followed some oing research and found other areas where longer term research is uired. These will be documented in more detail later this year as indied in Item No. 7 above. A brief listing of several of these items follow

Hydrogen Embrittlement. - This work is leading to an understanding of the problem and should be continued. Better control and reporting of experimental variables is recommended.

Hydrogen Dispersion After a Gas Leak or Liquid Spill. - It is time to extend the original experimental work done over two decades ago. The NASA tests mentioned earlier are a start on this but will be too small. Eventually, larger tests must be performed. This will be expensive and could be a joint venture between the DOE and NASA. The tests should study the effects of the size, mode, and rate of leak on the dispersion and concentration and temperature distributions in the vapor cloud.

Hydrogen Combustion. - A study should be made of the effects of size, rate, and mode of leak, confinement, impurities, strength and distribution of ignition source on the transition of deflagration (burning) to detonation (explosion).

Risk Analyses. - A risk analysis should be made for transmission of gaseous hydrogen by pipeline and also means should be sought to improve the risk analysis for the transport of LH_2 as more data become available.

Hydrogen Detectors. - Improved models are needed having greater simplicity, durability, versatility and lower cost.

Oxygen By-Product. - A study is desirable of methods of obtaining environmental benefits from the generation of large quantities of oxygen as a by-product of hydrogen production.

Cryogenic Storage Vessel Code. - Efforts should be made to have one of the code making bodies start to develop a cryogenic storage vessel code.

appliances.

9. Water in Stratosphere. - A study should be made to determine whether any adverse environmental impact will result from the water deposited in the stratosphere by a fleet of hydrogen fuel SSTs.

8. CONCLUSION

Hydrogen is already in use on a scale that, though small compared to tal takeover, is large enough to demonstrate the maturity of the tech-logy. It can be handled safely, a fact attested to by over 60 years of ga stribution and over 25 years of LH_2 usage. Much of the previous excellent fety record can be credited to having a good knowledge of the properties a havior of hydrogen before going into large-scale use. There are sufficien des and regulations for present usage.

However, to handle hydrogen, or any other fuel safely, it is necessar understand the basic phenomena that could lead to a mishap, and to have a owledge of the limits to the consequences of any mishap. Once these are own, it is possible to establish the proper procedures and necessary con-ols. A similar sequence is desirable for the control of pollution.

There is good reason to believe the use of hydrogen will continue to crease. A number of research problems necessary for fully realizing safe d environmental benefits have been identified. Now is the time to start is research.

REPORT V

Ammonia - Environmental and Safety Concerns

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Prepared for the
Division of Environmental Control Technology
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under Contract EY-76-C-06-1830

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REPORT V

TABLE OF CONTENTS

TABLES

SUMMARY

Interest by the government and the ammonia industry in the safety as handling, storing, transporting and using ammonia has led to a propose dy of ammonia spills, both pressurized and cryogenic, in both land and ironments. The study enjoys the support of The Fertilizer Institute (affiliate members, and several governmental agencies: the United Sta st Guard, the Federal Railroad Administration, and the Department of E objectives of the spill study are to determine the dispersion behavio onia from both pressurized and cryogenic releases, to improve models cribing this behavior and to provide experimental data on the extent o ard posed by ammonia vapors. Such characteristics as size and shape o vapor cloud, ammonia concentration profiles, and vapor buoyancy will estigated, as will the effects attributable to varying release conditi weather stabilities. This is a status report on a white paper being tten in preparation for this study; it will identify the environmental ety issues of ammonia as an energy source and document previous work o subject. It is expected that the white paper will be completed in ch 1979, and will contain the same major sections used here. Those se parentheses indicate the scope of work not completed at this time.

Ammonia is a natural part of the nitrogen cycle and, as such, life c st without it. However, in massive doses it is hazardous to all forms e. Ammonia is easily assimilated into the environment. Once disperse s not present any significant ecological problems. The basic concerns ociated with using ammonia are the safety aspects of production, trans n, storage and use. Two main concerns are the health consequences of osure and the possibilities of fire and explosions. Hence, the researc k in this industry may also be used to evaluate the environmental and ues related to using ammonia as a fuel.

Under ambient conditions, ammonia readily evaporates and it is also y soluble in water. The vapor, although lighter than air, still is of ected at considerable distances from accidental spills. In water, it atly increases the pH and the temperature; both of these factors are h rimental to aquatic life.

This report describes the properties, potential hazards, production methods, accident statistics, regulations and control techniques for ammoni This provides a foundation for assessing key environmental and safety issue and the research and development that needs to be performed.

PRESENT AND FUTURE USAGE AND SUPPLY

Ammonia is not presently in wide use as a fuel. However, it is con-
dered as a suitable substitute for hydrocarbons and the U. S. Army has
nducted a number of tests in conjunction with its "Energy Depot Concept
monia would be produced and used under field conditions. In addition,
e use of ammonia as a fuel for internal combustion engines has been
vestigated in Europe but very little information is available on the
bject.

When ammonia is combusted with air, the products are water and nitro
e heating value of ammonia is about 40% of gasoline. The stoichiometri
r-fuel ratio for ammonia is 6.06:1 as compared to a much leaner ratio o
out 14.5:1 for gasoline. Based on equal volumes of stoichiometric air-
el mixtures, the heat content of ammonia-air mixture is about 80% of
hat of the gasoline-air mixture. Thus in reciprocating type engines, t
ower produced would not exceed about 80% of that produced by gasoline
nd air mixture. Ammonia does have a high octane rating (greater than 1
esearch octane number) and this is an advantage. This would permit hig
ompression ratios and the use of a supercharger, both of which signific
mprove performance. The heat of vaporization of ammonia is 4.4 times t
f gasoline and the engine consumes 2.4 times as much fuel by weight for
qual power outputs. Therefore, ammonia requires 10.3 times as much hea
f vaporization as gasoline. A vaporizor would therefore be necessary
mmonia were to be used as a fuel.

The current major uses of ammonia are for fertilizer and associate
products. In 1976, 15.2 million metric tons of synthetic anhydrous amm
were produced in the United States. Approximately 80% of this ammonia
used as a direct application fertilizer and in the production of other
fertilizer products such as urea, ammonium nitrate and ammonium phospha
The remaining ammonia was used to manufacture non-fertilizer materials
such as ammonium nitrate for explosives, urea for animal feeds and res
nitric acid, acrylonitrile and various amines.

taken from the air. The hydrogen may be obtained from a number of sour 1) Natural gas, 2) petroleum, 3) coal, 4) by-product of chemical opera and 5) electrolysis. In the United States, 98% of the synthetic ammon is produced by steam reforming natural gas to produce the hydrogen. Th remaining 2% is produced using hydrogen from electrolysis cells in chlo caustic soda plants. There are six major steps when natural gas is use as a feedstock: 1) natural gas desulfurization, 2) catalytic steam re ing to produce hydrogen, 3) carbon monoxide shift to produce more hydro 4) carbon dioxide removal, 5) methanation to convert residual carbon d to methane, and 6) ammonia synthesis. The first, third, fourth and fi steps are designed to remove impurities such as sulfur, CO, CO_2 and wat from the feedstock, hydrogen, and synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen is introduced into the proc The sixth step produces anhydrous ammonia from the synthesis gas. The second step is an endothermic reaction; additional energy is required produce steam. Hence, about 25% to 35% of the natural gas is used as for these purposes while the remaining is used as the feedstock. Many have had to switch to No. 2 fuel oil for these purposes during the wint months when natural gas supplies are curtailed.

In other parts of the world, coal and naptha are effectively used feedstocks for producting hydrogen. In a number of areas, natural gas less expensive than in the United States. In these cases ammonia is pr and then shipped to the United States. Currently, the U. S. productio capacity is growing about 4 to 8% per year, yet the increase in imports is causing a slack in production. Further increases in the price of na gas will seemingly complicate this matter further.

Anhydrous ammonia is ordinarily stored and handled as cryogenic l (-33° C at 1 atmosphere). In a few cases, ammonia is stored at about and some ammonia is evaporated to keep the liquid cooled; in these case the vented ammonia is usually compressed and condensed or absorbed in w to make by-product aqua ammonia.

ailcars (up to 130 m^3), barges or pipelines. In the last decade two ma
ipelines have been constructed: 1) the Mid-American Pipeline system
oing from Texas to Minnesota through Oklahoma, Kansas, Nebraska and Iow
nd 2) the Gulf Central Pipeline system going from Louisiana to Nebraska
nd Indiana through Arkansas, Missouri, Illinois and Iowa.

(This section will describe the sources and sinks of ammonia and indicate how ammonia is a part of the nitrogen cycle. The fate of ammonia in soil, water and atmospheric environments will be described. Known ecological effects and human health effects will also be included. A portion of this material is included below.)

The effect of ammonia can range from a mild irritation to severe attack of sensitive membranes of the eyes, nose, throat, and lungs, depending on the concentration. Because of its great affinity for water, it is particularly irritating to moist skin surfaces. The physiological effects of ammonia are summarized in Table 1. Liquid ammonia vaporizes rapidly when exposed to the atmosphere and it will absorb heat from anything it contacts so when it touches the skin it can freeze the tissue and cause "freeze burns" that are similar to regular burns.

Table 1 Physiological Effects of Ammonia

Concentration, ppm	Effects
20	first perceptible odor
40	a few individuals may suffer slight eye irritation
100	noticeable irritation of eyes and nasal passages after a few minutes exposure
400	severe irritation of the throat, nasal passages, and upper respiratory tract
700	severe eye irritation; no permanent effect if the exposure is limited to less than 1/2 h
1700	serious coughing, bronchial spasms, less than 1/2 h of exposure may be fatal
5000	serious edema, strangulation, asphyzia; fatal almost immediately

ACCIDENTAL SPILLS

(This section will contain a compilation of ammonia spills durin production, storage, transportation and use. A portion of this secti follows.)

TRANSPORTATION

During the period 1971-1975, 239[(a)] incidents involving transporta accidents with anhydrous ammonia were reported to the U.S. Department Transportation. From 1971 to April 1977, there were 61 incidents tha injury or death related to the handling or transportation of anhydrou ammonia.

Quantities too small to be measured (owing to pressure release b a safety-valve shutoff caused by defective or accidentally ruptured f valves or by closures of the container) are the predominant cause of during transportation of anhydrous or aqua ammonia. Usually, hospita is not required--the injured having received exposure sufficient to c eye irritation, minor skin burns, or fume inhalation--and the injured released after treatment.

A number of accidents involving the transportation of anhydrous monia have resulted in injuries and death from exposure to it. Some dents involved transfer of the product at storage facilities or trans by truck, train, and pipeline.

In 1976, during the unloading of a tractor-trailer at a bulk sto plant, a 2-in. (5-cm) liquid transfer hose burst. The failure of the devices to shut down resulted in the discharge of 5,500 gal (14.2 t) anhydrous ammonia. Nine townspeople were treated for inhalation of t fumes and released. Two persons who assisted in the rescue had to be hospitalized, owing to exposure to the fumes.

(a) Data from Office of Hazardous Materials Operations, U. S. Department Transportation, Washington, D.C.

in Indiana, the driver had completed unloading, had bled off the pressure and had disconnected the hoses and laid them on the ground. While capping the unloading pipe, he accidentally opened the valve for the unloading line allowing the anhydrous ammonia between this valve and the safety valve to escape. He was not wearing safety clothing. He ran to a water tank and placed his head and shoulders in the water. By the time a witness ran to him, he was limp; he never regained consciousness.

In 1973, a cylinder used in servicing air-conditioning equipment and containing 2.2 gal (5.7 kg) was being transported in the cargo space of a half-ton van truck. The cylinder ruptured (for unknown reasons) as the truck was moving at approximately 60 mph on a freeway in Industry, California. The driver stopped the truck, opened the door, and fell out. Although attended by highway patrol and a fire rescue squad, he died either at the scene or en route to the hospital.

A catastrophic accident involving a truck occurred in May 1976 in Houston, Texas, when the semitrailer containing 7,509 gal (19.3 t) of anhydrous ammonia overturned owing to the lateral surge of the liquid and excessive speed of the truck on a curve of a freeway overpass, and plunged 15 ft to the freeway below. The truck's tank ruptured and one of the overpass support columns was damaged. A 100-ft high cloud of ammonia developed. Rescue was hampered by the absence of wind under the overpass, which prevented the dispersion of the gas; the danger persisted for appsoximately 2 1/2 hr. Five deaths and 178 injuries were caused by inhalation of the ammonia fumes.

An accident involving two trains occurred in Glen Ellyn, Illinois, in May 1976. It was caused by a faulty outside rail of a curved track that did not comply with federal track safety standards. The locomotive and 27 cars of a freight train overturned, owing to the lateral force on the faulty track. When a second train traveling in the same direction on an adjacent track collided with the derailed train, a tank car in the second train ruptured, releasing 20,000 gal (51.5 t) of anhydrous ammonia. The accident occurred in the early morning, and 3,000 residents were evacuated and kept away for more than 16 h. There were no deaths, and the injuries suffered by 15 people were not serious.

Some 8,800 gal (22.7 t) of anhydrous ammonia leaked from the tank ca
a train over approximately a mile of track in Reese, Michigan, in Apr
76. The accident occurred when a train unloaded one of its cars onto
ack where the tank car was being unloaded. The cars coupled, and the
ctor pulled the cutting lever and signaled the engineer; however, the
iled to uncouple, and the discharge pipes on the tank car were pulled
lling the hoses apart. Local residents were notified to evacuate, and
ly two people were injured.

In February 1969, a catastrophic train accident occurred in Crete,
braska. A train derailed on a curve, and the derailed cars struck cars
anding on a siding; a tank car was fractured by the impact and released
,200 gal (75.2 t) of anhydrous ammonia. At 6:30 a.m., when the acciden
curred, the temperature was 4° F (-15.6° C), and there was ground fog,
th thin scattered clouds at 12,000 ft and no wind. A temperature inver
on had occurred in the area. Several houses close to the railroad were
maged by flying parts from derailed cars and from the burst tank car.
ose houses quickly filled with ammonia gas, forcing the residents to
andon them and try to escape. Several residents of other houses smelle
e gas, left their homes, and sought shelter. Any person who ventured i
e vapor cloud without adequate protection was either killed or seriousl
jured. Five people were killed immediately by ammonia, another died la
d 53 were injured (28 of them seriously).

The anhydrous ammonia pipeline of the Mid America Pipeline Company
APCO) ruptured at Conway, Kansas, in December 1973, releasing 89,800 ga
31.1 t) of anhydrous ammonia into the atmosphere. The accident was cau
excessive pressure due to the failure of a remote-controlled valve to
en when the station at Borger, Texas, began pumping. Pumping was stopp
ter 9,660 gal (24.9 t) of anhydrous ammonia had been pumped into the li
d the indicator light on the console in Tulsa, Oklahoma, still showed t
e valve had not opened. The 8-in. (20.3-cm) pipeline ruptured under an
itial pressure of at least 1,200 psig (8,275 kN/m^2). At the time of th
cident, the ground was covered with snow, ice, and sleet. The temperat
s near 20°F (-7°C), the sky was clear, and the wind was at 5-10 mph.

injured were the drivers of two trucks on U.S. Highway 56, within a half-
(0.8 km) of the ruptured line; they were hospitalized because of ammonia
s to the eyes, nose, throat, and lungs. The ammonia vapor was visible a
f-mile from the leak, and invisible but very irritating to the eyes, nose,
throat for another 3.5 miles (5.6 km). Beyond that point, ammonia odor
detectable for another 4 miles (6.4 km), but did not irritate the eyes,
e, or throat.

According to U.S. Coast Guard records for the period 1971 to mid-1977,
accidents or spills involved tank barges, rather than ships, and involved
tly spills from leaky fittings, valves, or hoses during transfer. During
s period, the only catastrophic accident occurred in October 1974. A
ge containing 9,000 tons (8,166 t) of anhydrous ammonia and 4,500 (4,083 t
bulk urea broke from the towline during a storm and grounded and sank off
ur Peninsula, Baranof Island, Alaska. The entire cargo of anhydrous ammon
urea escaped to the marine environment and the atmosphere. There was no
osure of humans. Some mussels and starfish died, and approximately a
are mile (2.6 km^2) of forest in the immediate vicinity was laid waste by
onia fumes.

Reports involving the overturn of nurse tanks[(a)] on the highway or invol
other vehicles can be found in newspapers and police records, but usually
icate a small envelope of danger with few injuries, in most instances
olving only the driver or people engaged in rescue or cleanup. Statistics
such accidents appear to be unobtainable.

In agricultural areas, local doctors are seeing the results of on-the-
n exposure of farmers to ammonia. Reports of accidental exposure to a
imal envelope of danger (a spray of liquid, ruptured hose, leaky valve,
.) have involved loss of eyesight, respiratory problems, and skin burns.

Small tractor drawn tanks used to transport ammonia from distributor's
storage tank to the farm.

A 16-year-old employee of an anhydrous ammonia distributing company
injured while transferring liquid from a rail car to a nurse tank. Th
loyee was standing on the side walkway of the rail car. The nurse tank
led more rapidly than expected; before the employee realized how full i
, the safety relief valve emitted a spray of ammonia. (This valve is
igned to prevent the tank from being overfilled--it relieves at 85% of
acity--and ensures that there is space for the anhydrous ammonia to
and when the temperature rises, without bursting the tank.) The victim
nding about 6 ft above the valve, was sprayed on the face and chest. H
ediately jumped to the ground and began to wash his face in a water tan
t was on the premises for such emergencies. He was taken to a local
pital, but quickly transferred to a larger hospital. Facial burns were
extremely serious, and both eyes were unaffected; but pulmonary edema
umonitis resulting from inhalation developed quickly, with inflammation
edema of the upper airways. A tracheostomy was performed, and aspira-
n was necessary. Treatment included pressurized oxygen, aminophylline,
several antibiotics. Recovery was gradual, and the patient was dis-
rged after 11 days in the hospital. There was no residual lung damage.

A 17-year-old farm boy who applied fertilizer for a commercial concer
injured during transfer of aqua ammonia (25% ammonia in water). He an
employer were installing a new transfer pump when the accident occurre
n the new pump in place, they started to move the liquid from the nurse
k to the applicator tank. One hose had not been tightened sufficiently
began to leak. Without shutting off the machine, the boy grasped the
e and began to rotate it to make a tight connection. As he did so,
opposite end of the hose flipped out of the applicator tank and spraye
with several gallons of aqua ammonia. Knocked down but not panicking,
scrambled to his tractor and used his jug of water to wash his eyes. H
n ran 70 yards to a nearby creek and immersed himself, but he did not
ove his ammonia-soaked clothing. He noted some tightness of his throat
ing the first few minutes after the accident. He was driven home by hi
loyer, removed his clothing, and rested. He soon noticed, however, tha
had received burns to the buttocks from contact with his clothing durin
2-mile ride home. Taken to a local hospital, the victim was treated

for second degree burns and recovered completely within a few days. No eye injury was sustained.

A 36-year-old manager of an anhydrous ammonia retail operation was injured in a farmer's field to which he had been summoned because of improperly functioning equipment. The farmer was using a 1,000-gal (3.8-m^3) nurse tank connected by direct supply to a seven-row tool bar applicator. Anhydrous ammonia runs from the nurse tank through a hose and quick-coupling device to a flow regulator on the tool bar and from there out through the individual knives into the ground. The coupling device had been leaking, so the manager installed a new one. When the new device was tested, by opening the liquid-out valve at the supply tank and permitting ammonia to pass through the hose, leakage occurred again. The man closed the liquid-out valve and attempted to make a tighter connection by jiggling the coupler. The coupler flew apart, and the man was sprayed in the face with anhydrous ammonia that had remained under pressure in the portion of the hose between the coupler and flow regulator. Immediate blepharospasm prevented him from seeing clearly as he got away from the escaping ammonia stream. The farmer who was with him at the time took him to the rear of the nurse tank and helped him pour a 5-gal emergency water supply over his face. He washed with water from a Thermos bottle while being driven 25 miles to a doctor's office, where his eyes were irrigated for several minutes. During the washing, the victim concentrated on the left side of his face, believing that only that part had been affected. His right eye, which in fact had also been sprayed, was thus somewhat neglected and sustained the greater damage, with resulting irritative conjunctivitis and superficial corneal ulceration. Second-degree facial burns were also sustained, and palpebral edema of the left eye developed of such magnitude as to swell the eye shut several times during the following week. Recovery took a week, and there were no known sequelae.

ENVIRONMENTAL & SAFETY STANDARDS

(This section will contain a compilation of standards that apply to roduction, storage, transportation and use of ammonia. In addition, an nvironmental standards will also be described.)

Dikes can probably be used to contain spills from ruptured tanks; s ikes are required or standard practice in the storage of petroleum proc nd other hazardous liquids. More expensive double-wall construction mi lso be considered. Whatever the design or method, the principle of con ainment in case of natural or accidental release of ammonia into the en onment, where it would flow to the nearest water-course, should be cons imultaneously with the release of the liquid there will be vapor format o the location of storage with respect to surrounding residential areas hould be considered. Safe distance figures are found in American Natic tandard K61.1-1972, subsection 2.5, "Location of Containers," paragraph .5.4. Container locations are to comply with Table 2, according to 61.1-1972.

The pressure tanks used for storage of ammonia and delivery to the onsumer and farmer may vary in capacity from a few gallons to thousands allons and are manufactured with a minimal design pressure (working pre f 250 psig per the ASME (American Society of Mechanical Engineers) con- truction code for unfired pressure vessels. Although these tanks are esigned for a maximal working pressure of 250 psig (about 1,720 kN/m^2), ney are hydrostatically tested at the time of manufacture to about 1.5 imes the design pressure, or about 375 psig (2,580 kN/m^2). The interna ressures of stored anhydrous ammonia in these tanks may vary according emperature.

The tanks are also to be equipped with pressure-relief valves (Amer ational Standard K61.1-1972, subsection 2.9, "Safety Relief Devices"), irect the vented material away from the container upward and without ob truction to the atmosphere. Such devices, to operate with relation to esign pressure of the container, are as listed in Table 3.

TABLE 2

Safe Location of Ammonia Containers[a]

Nominal Capacity of Container, gal (m^3)	Minimal Distance, ft (m), from Container to: Line of Adjoining Property that May Be Built on Highways and Main Line of Railroad	Place of Public Assembly	Institution Occupancy
Over 500 to 2,000 (over 1.9 to 7.6)	25 (7.6)	150 (46)	250 (76)
Over 2,000 to 30,000 (over 7.6 to 114)	50 (15)	300 (91)	500 (152)
Over 30,000 to 100,000 (over 114 to 379)	50 (15)	450 (137)	750 (229)
Over 100,000 (over 379)	50 (15)	600 (183)	1,000 (305)

[a]Data from American National Standard K61.1-1972, paragraph 2.5.4.

TABLE 3

Start-to-Discharge Pressures of Relief Devices of Ammonia Containers[a]

Containers	Relief Pressure, % of Container Design Pressure	
	Minimum	Maximum
ASME-U-68, U-69	110%	125%
ASME-U-200, U-201	95%	100%
ASME 1952, 1956, 1959, 1962, 1965, 1968 or 1971	95%	100%
API-ASME	95%	100%
U. S. Coast Guard	as required by USCG regulations	
DOT	as required by DOT regulations	

(a) Data from American National Standard K61.1-1972, paragraph 2.9

rage and Handling of Anhydrous Ammonia, a consensus standard, also cove
y other topics, including first aid and personal protection equipment a
use, identification and marking of equipment, operational procedures,
ation of containers, various kinds of storage containers (including
rigerated and portable), transport systems mounted on trucks, and farm
lication.

The Code of Federal Regulations (CFR 29-1910:111) establishes require
ts for the storage and handling of anhydrous ammonia. Section (a)
tes that this standard is intended to apply to the design, construction
ation, installation, and operation of anhydrous ammonia storage systems
not to manufacturing or refrigeration plants where ammonia is used as
efrigerant. Section (b), "Basic Rules," deals with such items as
roval of equipment and systems; requirements for construction; original
t and requalification of nonrefrigerated containers; marking of nonre-
gerated and refrigerated containers; container appurtenances; piping,
ing and fittings; hose specifications; safety relief devices; charging
containers; tank car unloading points and operations; liquid-level gaug
ice; painting of containers; and electric equipment and wiring. Sub-
tion (10) of this portion of the requirements mentions training of pers
and specifies personal protective devices, including first aid water
plies for permanent and transport vehicles, except the farm applicator.
ationary storage installations must have an easily accessible shower or
gal--0.2-m^3--drum of water available, and each vehicle transporting
onia in bulk must have a container carrying 5 gal--0.02-m^3-- of water a
ll-face mask.) Section (c) describes systems that use stationary nonr
gerated storage containers; Section (d), refrigerated storage systems;
tion (e), systems that use portable DOT containers; Section (f), tank
or vehicles for the transportation of ammonia; Section (g), systems
nted on farm vehicles other than for the application of ammonia; and
tion (h), systems mounted on farm vehicles for the application of ammon
cific points and requirements are made concerning the safe handling and
ement of ammonia in these sections to minimize or eliminate the develop
t of hazards related to liquid or gaseous ammonia.

SAFETY AND ENVIRONMENTAL CONTROL PROCEDURES

(This section will outline the procedures that have been develop
handling spills during production, storage, transportation and use of
ammonia. In addition, hazard assessment methods will be identified.)

SAFETY AND ENVIRONMENTAL CONTROL ISSUES

(This section will draw on the material from the previous sectio
identify and define the issues associated with the use of ammonia as

BIBLIOGRAPHY

(This section will contain all of the references for the materia
given in this status report plus all of the additional material added
the final report.)

end Subtitle

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s may be directed to them at the address in box 12.

ract
e DOE Assistant Secretary for Environment has responsibility for identif
erizing, and ameliorating the environmental, health, and safety issues a
concerns associated with commercial operation of specific energy systems
r developing a safety and environmental control assessment of liquefied
as identified as a result of discussions with various Government, indust
demic persons having expertise with respect to the particular materials
d: LNG, LPG, hydrogen, and anhydrous ammonia. A program to address the
t issues has evolved.
e goal of the Program Plan (Section II) is to gather, analyze, and disse
al information that will aid future decisions by industry, regulators, a
relating to facility siting, system operations, and accident prevention.
h complements related programs supported by other Government agencies ar
y.) To accomplish the goal, three specific objectives have been identif
d predictive capability; verified prevention methods; verified control m
epth preliminary assessment will identify or confirm information needs.
d plan to acquire this information will be prepared. Appropriate elemen
c to each energy material will be selected from this list: vapor genera
ion; fire and radiation hazards; flame propagation; release prevention;
; instrumentation and technique development; scale effects experiments;
mental and ecological impacts; human health studies.
is report is a compilation of technical papers presenting progress in th
.

Words
ied gaseous fuels
effects experiments
generation   flame propagation
dispersion   instrumentation
propagation   release prevention

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